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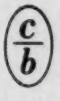

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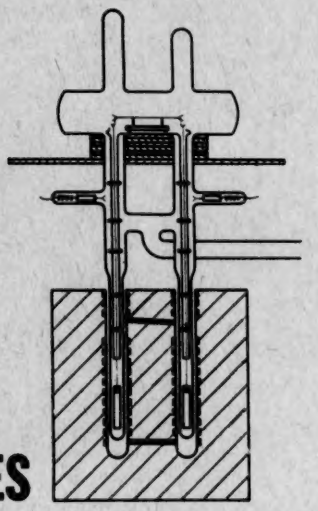

VOLUME I

VACUUM MICROBALANCE TECHNIQUES

Proceedings of the 1960 Conference Sponsored by
The Institute for Exploratory Research
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U. S. Army Signal Research and Development Laboratory
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Introduction by
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The proceedings of this conference provide an authoritative introduction to the rapidly widening scope of microbalance methods which is not available elsewhere in a single publication.

The usefulness of microbalance techniques in the study of the properties of materials lies in their extreme sensitivity and versatility. This renders them particularly important in studies of properties of condensed systems. In addition to the historical use of microbalance techniques as a tool of microchemistry, they have, in recent years, found extensive application in the fields of metallurgy, physics, and chemistry. The uniqueness of the method results from the facility it provides in making a series of precise measurements of high sensitivity under carefully controlled conditions over a wide range of temperature and pressure.

This significant new volume contains papers in three major categories. The first group of reports deals with the general structural features and measuring capabilities of microbalances. In the second group, a sophisticated consideration and much needed evaluation of sources of spurious mass changes associated with microbalances is presented. The third group describes some of the most recent extensions in microbalance work to new research areas such as semiconductors, ultra-high vacuum, and high temperatures. These papers provide an interesting account of advances in the application of the microgravimetric method to three new and important fields of research on the behavior of materials.

170 pages **$6.50**

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INCREASING THE SENSITIVITY OF DETERMINING ELEMENTS IN A FLAME

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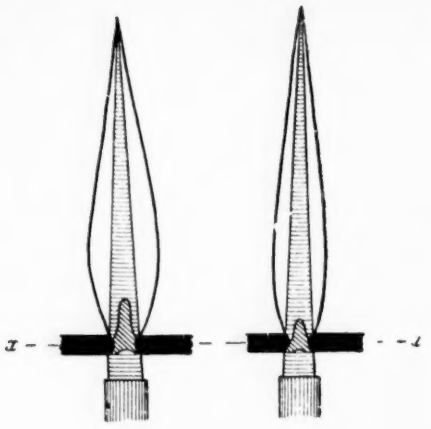
Despite the fairly high sensitivity of the flame photometric method, particularly for the determination of relatively readily excited elements, and the widespread use of this method in modern analytical chemistry, practical demands, in particular, those of geochemistry and chemical technology, require that the sensitivity of the method be increased further, and that it should be applicable to the determination of a larger number of elements. Since the sensitivity of the method is determined finally by the ratio of the value of the useful signal in the recording setup to the background (or, more accurately, by the fluctuations in the background*), in principle, there are two possible methods of solving this problem. The first of these methods—increasing the relative (compared with the background) intensity of the useful signal—is related to the presence of a minimum amount of the test element in the test material. This can be achieved by increasing the flame temperature and adopting a number of measures relating to preparing and introducing the test solutions into the flame, measures which taken together would increase the number of atoms emitting radiation per unit time in the source. The second method would be, in essence, to decrease the background and increase its stability, by using more advanced spectral equipment characterized by a higher resolving capacity, and to improve the system used for recording the intensity of the analytical lines of the test element. Under such conditions one would expect an increase in the accuracy and selectivity of the determination as well.

Many papers have been published recently describing work carried out along both these lines: the use of flames with higher temperatures [2, 3], and the use of more advanced optical apparatus and apparatus for recording the spectra [4, 5].

The present article is devoted to results of studies carried out in our laboratory.

Combined Sources of Spectra Excitation. One of the possible ways of increasing the source temperature for carrying out quantitative spectrographic analysis in a flame would be to set up combined sources, flame-spark or flame-arc. The possibility of increasing the sensitivity of the spectrographic determination of certain elements by means of a flame-spark source has already been pointed out [6,7]. Nevertheless, the lack of published information on the properties of the first of these sources, coupled with the fact that the second source has not been studied at all, necessitated more systematic studies. The arrangement of both the spectra excitation sources studied is shown schematically in Fig. 1 (a and b). The ac arc or the spark fed from a DG-1 generator, were fixed horizontally and were ignited crosswise through the flame at a height of 10-15 mm above the top of the burner. Copper electrodes 7 mm in diameter were used. Carbon electrodes are unsuitable because of a strong increase in

*On this basis, Al'kemade [1] for example, suggests that the sensitivity of the method should be regarded as that concentration of the test element which gives a deviation (reading) in the recording apparatus equal to the experimental error in reading the scale.



a b

Fig. 1. Combined excitation sources. a) Flame–arc; b) flame–spark.

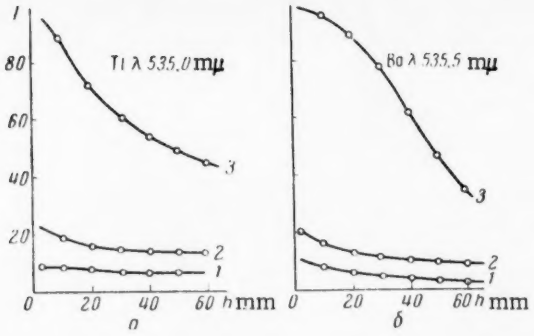


Fig. 2. The relation between the intensity of the analytical lines of Tl (a) and Ba (b) and the height (h) above the level X – X (Fig. 1) in different sources. 1) Flame; 2) flame–spark; 3) flame–arc.

background. The analytical gap was 6-9 mm. The current supplied to the arc was 3 amp, while that supplied to the spark was 2 amp. The spectrographic apparatus used was an ISP-51 spectrograph, the camera of which had F = 270. The spectra were recorded photographically ("Infra-760" and "Isochrome" plates with a sensitivity of 45 GOST units), and by means of a photoelectric setup* with a photomultiplier using an integrating scheme similar to that described by other authors.

In Fig. 2 are shown some of the curves obtained in this way; they illustrate the relation between the intensities of the analytical lines of various elements, and the height of the part of the flame being photometrically measured above the level at which the arc or the spark of the combined source is located. The curves shown are those of the analytical lines Ba (λ = 553.5 mμ) and Tl (λ = 535.0 mμ). Curves similar in appearance were also obtained for other elements. (Ga, In, La, and Yb). As is evident, the intensity of the analytical lines of the elements in a combined source is considerably greater than that in a flame. At the same time, the efficiency of a flame–arc source is higher in all cases (the intensity of the analytical lines is higher) than that of the second combined source. In the case of Ba the line intensity in a flame–spark source is 2-6 times that in a flame, while the line intensity in a flame–arc source is 6-25 times greater. The corresponding values for Tl are 1.7-2.5 and 5-9 times respectively.

Unfortunately, in parallel with the increase in the intensity of the analytical lines of the elements in the combined sources, there is also a strong increase in the background intensity, which, on using a photometric method of recording, as a rule**, makes it impossible to use the advantages indicated above of the combined sources (Fig. 3). In order to overcome this difficulty it would be necessary to use a discriminating scheme of recording the spectra. The simplest prototype of such a scheme would be, for example, a photographic plate whose sensitivity with respect to a weak background would be much less than its sensitivity to the most intense spectral lines. In this case, the combined sources of spectra excitation described above for increasing the sensitivity of the determination of certain elements would prove efficient enough used as they are.

In conclusion, we should like to point out that the combination of a flame with a higher temperature source – an ac arc or a spark – leads to an increase in the stability of these sources themselves (this is clearly shown in Fig. 4). It is possible that this could be used in spectrochemical research for developing an efficient method for introducing samples into the inter-electrode space of high temperature sources. Such a technique, which is an original analog of the well-known variants of the "spilling" method, in certain cases could, presumably, make it possible to increase the accuracy of the spectral determination of the elements.

*For a more detailed description of the operation of the photoelectric setup, see the following section of the present article.

**In the case of some elements (e.g., Ba), however, it is possible to find regions in the flame of the combined sources, for which $I_{line}/I_{background}$ approaches the value characteristic of a flame. In such cases, the significantly higher absolute intensity of the analytical line of the element in a combined source can be used for analytical purposes.

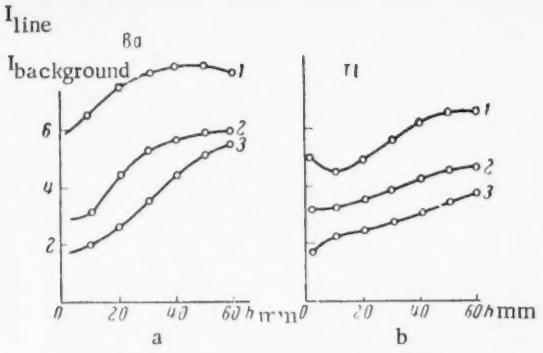


Fig. 3. The relation between the ratio $I_{line}/I_{background}$ and h for Ba (a) and Tl (b) in different sources. 1) Flame; 2) flame–spark; 3) flame–arc.

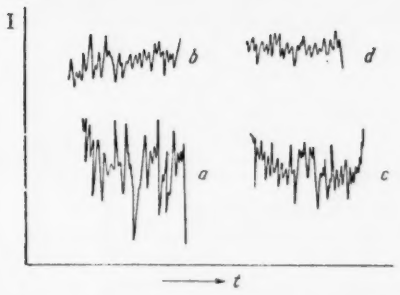


Fig. 4. The change in the intensity of the line Sr 460.7 mμ with time in different sources. a) Arc; b) flame–arc; c) spark; d) flame–spark (recorded on an EPP-instrument).

Recording Flame Spectrophotometer. With the aim of studying the second approach mentioned above for increasing the sensitivity of the determination of elements in a flame, we assembled a recording spectrophotometer. The setup is shown schematically in Fig. 5. It is assembled in the main from ready made units turned out by Russian industry. An ISP-51 spectrograph is used as the spectral apparatus. The FEP-1 recorder is used for taking and recording the spectra; it is designed for recording combination scattering spectra in the wavelength range 380-600 mμ.

The linear dispersion of the setup for λ = 4713 A is 32 A/ mm, which is close to the linear dispersion of the ISP-51 apparatus fitted with a camera with F = 270 mm. The maximum amplification factor of the amplifier is 10^8. The chart tape speed could be varied from 60 to 9600 mm/ hr. The run-down time of the carriage in the recording potentiometer of the instrument we used was 2.5 sec.

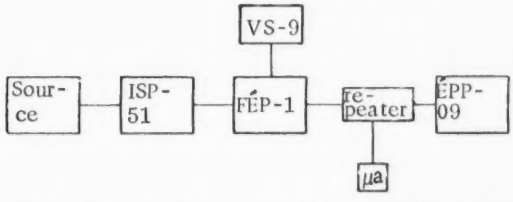


Fig. 5. Schematic diagram of the recording flame spectrophotometer.

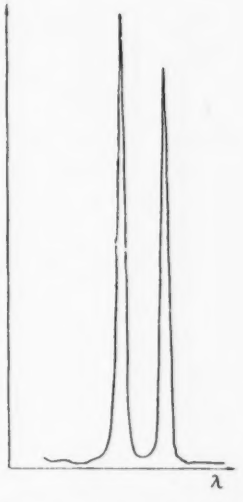


Fig. 6. Recording of the Na doublet 589.0-589.6 mμ on the spectrophotometer (slit width 0.025 mm).

The operating wavelength range indicated above is not quite suitable for flame photometry, since the analytical lines of a number of elements which it is desired to determine lie outside this range (lithium, potassium, rubidium, cesium). In order to extend the operating range of the apparatus, one of the spectrograph prisms (the small one) which is located near the output of the apparatus, was turned through a small angle, while another prism (also a small one) located near the input, was shifted through a certain angle in order to correct for the curvature of the line projected on the output slit of the apparatus. The angles through which the prisms were rotated were controlled so that the cesium line at 894.4 mμ fell within the operating range on the long wave side of the spectrum, while the magnesium band at

383 mμ fell within the operating range on the short wave side. Since the apparatus was rearranged in this way, additional focussing was necessary (on the basis of the maximum deviation of the potentiometer) on switching from the long wave side of the spectrum to the short wave side. There was no need for this focusing when determining high contents of the elements (i.e., when the value of the background was insignificant compared to the line intensity being measured), or on switching from photometric measurements of the parts of the spectrum in the cesium region (λ = 852 mμ) to the lithium region (λ =670 mμ) or from the thallium region (λ = 535 mμ) to the calcium region (λ = 422 mμ).

The FEU-18 (visible) and FEU-22 (red and infrared) photomultipliers were used for recording the light flow. Because the voltage supplied to the photomultiplier in the FEP-1 was not high enough (about 1000 v), and because of the large dark currents of the FEU-22 photomultiplier (difficult to compensate by the circuit), and the appreciable characteristic "dark" current of the amplifier of the setup, it proved inconvenient to use the amplifier and rectifier supplied with the apparatus. Instead of these, for supplying the apparatus, we used a VS-9 rectifier and

TABLE

Element	Line or band, mμ	Sensitivity, μg/ml	Element	Line or band, mμ	Sensitivity, μg/ml	Element	Line or band, mμ	Sensitivity, μg/ml
Lithium	670.8	0.0005	Magnesium	383	0.1	Barium	553.5	0.08
Sodium	589.6	0.0001	Cesium	852.9	0.003	Gallium	417.2	0.05
Potassium	769.9	0.001	Calcium	422.7	0.005	Indium	451.1	0.05
Rubidium	794.8	0.002	Strontium	460.7	0.005	Thallium	535.0	0.05

a cathode repeater, the circuit of which did not differ much from that used by Poluektov and Nikonova [4]. In the setup which we used, the input resistances were increased, and the resistances of the circuit used for compensating the dark current decreased in accordance with the lower value of the dark current of the actual photomultipliers used in our work. Standard connecting elements were used for linking up the various units of the apparatus; these elements made it possible to assemble the apparatus rapidly from the requisite parts, and enabled the photomultiplier anode to be switched to the amplifier or to the cathode repeater. When necessary, measurements could also be made on the basis of the readings on the galvanometer, for which purpose the latter was connected with the output of the cathode repeater or was connected into the photomultiplier in the usual way. Measuring apparatus with a sensitivity of 10^{-7}–10^{-8} amp/division or even a microammeter could be used in the cathode repeater circuit. The sensitivity of a determination will also be dependent on the characteristics of the measuring apparatus used.

At low concentrations of the test element, or in the presence of a large background, a small section of the spectrum (the line or the molecular band, and the adjacent background) can be recorded by means of the apparatus. It is convenient to record the spectrum at two standard rotation rates of the prism of the setup. The first permits the prism drum to rotate once in 12 min, while the second gives a rotation speed three times slower.

An acetylene-air flame was used as the excitation source. The burner, which was a Meker type, had a glass sprayer and a concave mirror which increased the sensitivity of a determination 2-3 times.

The apparatus described is characterized by a high light strength and dispersion. This enabled us, for example, to resolve the sodium doublet 589.6-589.0 mμ (Fig. 6) when the inlet and outlet slits had a width of 0.025 mm, while, by using narrow slits, it was possible to increase the selectivity of the photometric determination of elements considerably, and to decrease the flame background during the determination of calcium, strontium, magnesium, thallium, gallium, etc. The overall consequence of this is an appreciable increase in the sensitivity of determination in a flame.

An idea of the increase in sensitivity can be gained by examining the results presented in the Table.

The sensitivity of the determination of all the elements indicated is one order higher than that achieved hitherto [8]. Rubidium can be determined at this sensitivity in solutions in which the amount of potassium present is 100 times that of rubidium, while cesium can be determined in solutions in which the amount of potassium is 1000 times the cesium content; these are the conditions normally met during determination of these elements in natural materials. The sensitivity values given in the table may vary from 3 to 5 times, depending on experi-

mental conditions (slit width, the voltage supplied to the photomultiplier, the rate at which the solution is fed into the flame, etc), and, they indicate that it should be possible to determine a number of elements (e.g., cesium) without preliminary chemical concentration.

SUMMARY

With the aim of finding possible ways of increasing the sensitivity of the determination of elements in a flame, a systematic study has been made of combined sources: flame–arc and flame–spark. It has been shown that by using amplitude discriminators, or by recording the spectra on photographic plates, it is possible to attain a considerable increase in the sensitivity of the determination of these elements in these sources.

The design of a highly sensitive recording spectrophotometer for the determination of the elements in a flame is described; this spectrophotometer is assembled from the Russian equipment ISP-51 and FEP-1. Using this equipment it is possible to increase the sensitivity of the photometric determination of a number of elements by more than one order, and to determine these elements without their preliminary chemical concentration.

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POTENTIOMETRIC METHODS OF TITRATING MULTICOMPONENT MIXTURES OF ACIDS IN NONAQUEOUS SOLUTIONS

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Nonaqueous solvents [1-3], because of their characteristics, are valuable media at present for a large number of very important analytical determinations which cannot be carried out in aqueous solutions; the impossibility of carrying out such determinations in aqueous solutions is determined by the insolubility of many compounds in water, by small differences in pK values, by the dissociation of electrolytes in water, and, finally, by the leveling effect of water.

The same material can behave as a strong or a weak electrolyte, or as a nonelectrolyte, depending on the nature of the solvent, and behave as an acid, base, salt, or neutral compound.

The dielectric permeability [4, 5] and the chemical nature of the solvent [6] have an essential influence on the value of the electrical conductivity coefficient $\lambda / \lambda_0 = \alpha_1$, where λ is the equivalent electrical conductivity and λ_0 is the equivalent electrical conductivity at infinite dilution.

The primary state of a material in solution has been considered by many authors [7-12]. According to Izmailov [13-15], dissociation of electrolytes proceeds in several successive stages and is accompanied by the formation of solvates and by dissociation of the solvated interaction and association product of solvated ions (this is particularly true in medium characterized by a low dielectric permeability).

In the general case, the universal scheme of the dissociation process can be represented as follows, according to Izmailov

$$KA + (n + m)M \overset{I}{\rightleftarrows} KAM_n + mM \overset{II}{\rightleftarrows} K^+_{salt} + A^-_{salt}$$
$$\downarrow\uparrow\ III$$
$$+yM \overset{IV}{\rightleftarrows} K^+_{salt}A^-_{salt} + xM$$

The general equation, which reflects all the equilibria which are established in the medium of a given solvent, is expressed as follows:

$$K_{ord.} = \frac{K_{diss.}}{1 + K^*_{inst.} + K_{conv.}},$$

where $K_{ord.}$ is the electrolytic dissociation constant of the electrolyte as determined by the usual (ordinary) methods; $K^*_{inst.}$ is the equilibrium constant (I) expressing the formation of addition compounds between the electrolyte molecules and solvent molecules; the index [*] shows that K refers to an infinitely dilute solution; $K_{diss.}$

is the equilibrium constant (II) which expresses the dissociation of the addition product formed into ions; $K_{conv.}$ is the equilibrium constant (IV) which is the reaction constant for the conversion of the nonionized addition product into an ion pair.

The equilibrium constant (III) expresses the formation of ion pairs, $K^{-1}_{assoc.} = K^{-1}_{diss.} K^{-1}_{conv.}$ or $K_{diss.} = K^{-1}_{assoc.} K_{conv.}$

This equation can acquire various values for a number of special cases. Berg, Patterson [16], Correy [17], Sadek and Fuoss [18], and Kolthoff and Bruckenstein [19, 20] have derived analogous equations which are really special cases of the general equation.

The stronger the basic properties of a solvent, the stronger are its effect on weak acids. In basic solvents which have a high dielectric permeability and dipole moment, the strength of an acid increases. The stronger the acid properties of a solvent, the greater are its effect on weak bases. In acid solvents which have a high dielectric permeability and low autoprotolysis constants, the strength of a base increased. Thus, manifestation of acid or basic properties by the dissolved material is determined, not only by the dielectric permeability, but also by the chemical properties of the solvent.

Accordingly, the behavior of an electrolyte in a given solvent is determined not only by the properties of the electrolyte itself, but also by the properties of the solvent chosen. By choosing between solvents which possess different properties, it is possible to obtain solutions of electrolytes which behave differently. For example, the change in acid strength which occurs on switching from one solvent to another can be expressed by the following equation:

$$\Delta pK = pK_M - pK_{H_2O} = 2 \lg \gamma_{0\,ions} - \lg \gamma_{0\,molecule}$$

where, ΔpK is the difference between the pK values in the two solvents, e.g., in an organic solvent (M) and in water (H_2O); γ_0 are single activity coefficients relating to the state of the material in an infinitely dilute aqueous solution.

The basis of the theory of acid–base titration in nonaqueous solution has been developed by Izmailov [15].

The accuracy of a titration is determined by the ratio of the autoprotolysis constant (ionic product) of the medium K_i^* to the usual dissociation constant $K_{ord.}$ of the acid or base, $K_i^* / K_{ord.}$

The accuracy of a differential titration of acids or bases is determined by the ratio of their strength: $K_{ord.II}/K_{ord.I} = K_T$, where K_T is a titration constant which remains constant in an aqueous medium, but changes strongly with the solvent.

The smaller the value of K_T, the lower is the titration error. The limiting value of K_T should not exceed 10^{-4}. By choosing appropriate nonaqueous solvents it is possible to alter the ratios

$$\frac{K_i^*}{K_{ord}} \text{ and } \frac{K_{ordII}}{K_{ordI}},$$

considerably, so that it is possible to titrate materials in nonaqueous media which cannot be titrated in aqueous solutions.

The theory of the erros involved in the separate titration of mixtures of acids and bases has been developed by Roller [21]. Thus, the results and accuracy of acid–base titration depend not only on the titrimetric determination chosen, the titrant used, the concentration of the reactants, and the temperature of the solution being titrated, but also to a large extent on the character and nature of the solvent, which have a decisive influence on the strength of the acids and bases determined.

The work described here, which was based on the theoretical principles outlined above, was carried out with the object of developing methods for the differential titration of multicomponent acid mixtures.

EXPERIMENTAL

The acid mixtures were titrated by indicator, potentiometric, conductometric, and high frequency methods.

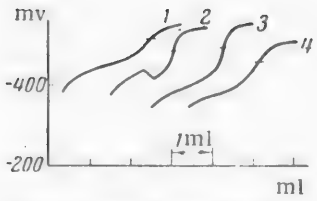

Fig. 1. Potentiometric titration curves for compounds which possess acid properties and cannot be titrated in water. 1) o-Cresol; 2) resorcinol; 3) α-naphthol; 4) pyrocathechol.

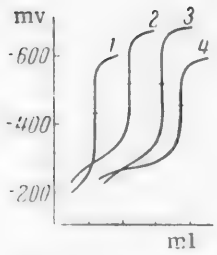

Fig. 2. Potentiometric titration curves for water insoluble acids. 1) Caproic acid; 2) caprylic acid; 3) pelargonic acid; capric acid.

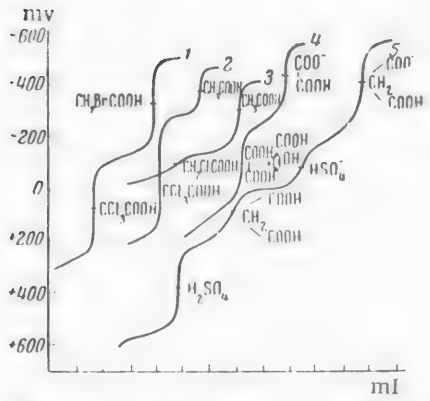

Fig. 3. Potentiometric titration curves for two component acid mixtures; 1) Trichloroacetic and bromoacetic acids; 2) trichloroacetic and acetic acids; 3) monochloroacetic and acetic acids; 4) salicylic and oxalic acids; 5) sulfuric and malonic acids.

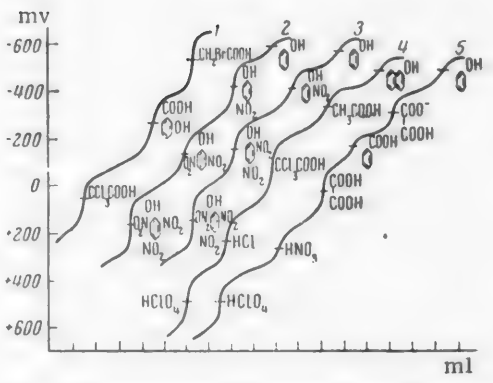

Fig. 4. Potentiometric titration curves for multicomponent acid mixtures. 1) Trichloroacetic + salicylic + bromoacetic acids; 2) picric acid + 2,6-dinitrophenol + p-nitrophenol; 3) picric acid + 2,4-dinitrophenol + o-nitrophenol + phenol; 4) perchloric acid + hydrochloric acid + trichloroacetic acid + acetic acid + β-naphthol; 5) perchloric acid + nitric acid + oxalic acid + benzoic acid + phenol.

As our work showed, the indicator method of titrating mixtures of acids has only limited application, since the presence of two or three (and sometimes a larger number) components in a mixture does not allow the possibility of choosing indicators, the color change ranges of which would correspond to the several equivalent points. Moreover, in strongly colored and oxidizing media, indicators cannot in general be used.

The potentiometric method permits determination of a large number of the components of mixtures in nonaqueous solutions. The high frequency is no direct contact between the solution and the electrodes; this is of particular importance for the titration of nonaqueous solutions. The fact that there is no direct contact means that it is possible to exclude the effects of polarization, adsorption, and oxidation–reduction reactions on the surface of the electrodes–effects which often distort the results of conductometric titration. Taking into account what has been said above, we decided to concentrate on two methods: potentiometric and high frequency. The work described here is devoted to the potentiometric determination of mixtures of acids. The titrant we used was tetraethylammonium hydroxide, which, as indicated earlier [22] has considerable advantages over other basic titrants. It dissolves readily in organic solvents and forms readily soluble salts with acids, while the glass electrode

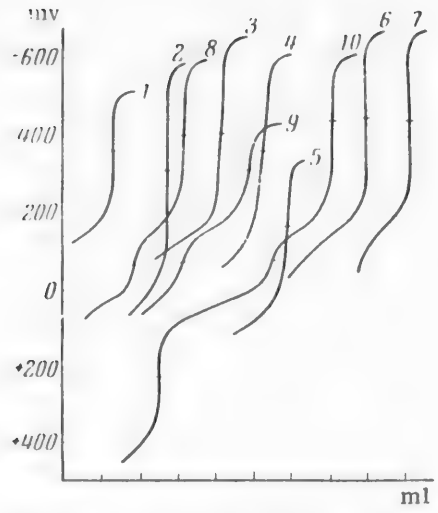

Fig. 5. Potentiometric titration curves of individual benzoic acid derivatives and their mixtures. 1) m-Hydroxybenzoic acid; 2) salicylic acid; 3) o-nitrobenzoic acid; 4) p-nitrobenzoic acid; 5) 2,5-dinitrobenzoic acid; 6) o-bromobenzoic acid; 7) p-bromobenzoic acid; 8) salicylic acid + benzoic acid; 9) salicylic acid + m-hydroxybenzoic acid; 10) sulfuric acid + salicylic acid.

Determination of Some Benzoic Acid Derivatives

Acids determined	Taken, g	Found, g	Error (relative), %
Salicylic acid	0.0343	0.0341	−0.6
m-Hydroxybenzoic acid	0.0484	0.0484	0.0
o-Nitrobenzoic acid	0.0227	0.0229	+0.9
p-Nitrobenzoic acid	0.0546	0.0550	+0.7
o-Bromobenzoic acid	0.0297	0.0295	−0.6
p-Bromobenzoic acid	0.0338	0.0341	+0.9
3,5-Dinitrobenzoic acid	0.0461	0.0464	+0.6
Salicylic +	0.0381	0.0383	+0.5
benzoic acid	0.0557	0.0555	−0.4
Salicylic +	0.0465	0.0469	+0.8
m-hydroxybenzoic acid	0.0623	0.0620	−0.5
Salicylic +	0.0412	0.0416	+0.9
sulfuric acid	0.0134	0.0135	+0.7

does not loose its sensitivity in its presence. The best results were obtained with a 0.1 M solution of tetraethylammonium hydroxide in a 5:1 mixture of benzene and methanol. At lower concentrations of the titrant the equivalence points are less sharp, while increases in the titrant concentration affect titration of acid mixtures unfavorably.

The acids were titrated in acetone, methyl ethyl ketone, methyl butyl ketone, and methyl benzyl ketone, which readily dissolved both the original materials and the materials formed during titration; in addition, they possess differentiating properties. Acetone and methyl ethyl ketone possess approximately equal differentiating properties, but the acid salts formed during titration are more soluble in methyl ethyl ketone. Methyl butyl ketone and methyl benzyl ketone were given less attention, since the first of these solvents usually contains a large number of detrimental impurities which have to be removed, while the second is too expensive.

The experimental technique and the preparation of the titrant have been described in [22].

The following compounds were titrated: phenol, acetic and benzoic acids and their derivatives, and also their mixtures with organic and inorganic acids.

Results for the titration of individual acids and their mixtures are given in Figs. 1-5. In Fig. 1 are shown the titration curves of compounds which cannot be titrated in water because of their low dissociation constants. Derivatives of phenol and naphthol possess very weak acid properties, so that it is impossible to establish the titration end point in aqueous media. In a methyl ethyl ketone medium the acid properties of these compounds increase, and such compounds as o-cresol, resorcinol, pyrocatechol, and α-naphthol can be titrated in nonaqueous media. Titration curves for the following acids which are insoluble in water are shown in Fig. 2: caproic, caprylic, pelargonic, and capric acids. In methyl ethyl ketone these compounds behave as relatively strong acids and so can be titrated in nonaqueous media.

A comparison of the titration curves of individual acids with the titration curves of their mixtures shows that in a methyl ethyl ketone medium, differential titration is possible in those cases where the beginning of the potential jumps of the individual acids differ by more than 100 mv. Thus, in the case of the titration curves of acetic acid and its chlorinated derivatives, the difference between the beginning of the potential jumps of acetic and trichloroacetic acids is 400 mv, while the difference between the potential jumps for acetic and monochloroacetic acids is 100 mv. Titration curves for acetic acid plus trichloroacetic and monochloroacetic acids are shown in Fig. 3 (Curves 2, 3).

Two clearly defined potential jumps are observed on the titration curve for a mixture of trichloroacetic and acetic acids; on the titration curve for a mixture of monochloroacetic and acetic acids, however, the potential jump corresponding to neutralization of monochloroacetic acid is not defined clearly enough. Trichloroacetic acid is a stronger acid than bromoacetic acid and can be determined in its presence (Curve 1).

Curve 4 corresponds to the titration of a mixture of a dibasic acid (oxalic acid) and a monobasic acid (salicylic acid). In a methyl ethyl ketone medium, salicylic acid is as strong as oxalic acid in its first dissociation stage. Accordingly, there are two jumps one the titration curve, one of which corresponds to neutralization of salicylic acid and oxalic acid to the first stage, while the second corresponds to the second stage in the neutralization of oxalic acid.

Two potential jumps are observed during the titration of sulfuric acid in a methyl ethyl ketone medium. This fact permits the determination of sulfuric acid in its mixtures with mono- and dibasic acids. Thus, during the titration of a mixture of sulfuric and malonic acids (Curve 5) four potential jumps are observed: the first corresponds to the first stage in the neutralization of sulfuric acid, the second to the first stage in the neutralization of malonic acid, the third to the secondstage in the neutralization of sulfuric acid, and the fourth to the second stage in the neutralization of malonic acid.

Titration curves of multicomponent mixtures are shown in Fig. 4. During the titration of mixtures of the three acids: trichloroacetic, salicylic, and bromoacetic acids, Curve 1 with three potential jumps is obtained. The first jump corresponds to completion of neutralization of trichloroacetic acid, while the second and third jumps correspond to neutralization of salicyclic and bromoacetic acids respectively. In methyl ethyl ketone, salicyclic acid is a stronger acid than bromoacetic acid, whereas in water both these acids have the same pK value of 3. Curves 2 and 3 were obtained during titration of mixtures of phenol and its nitro derivatives. Nitro groups enhance the acidity of the phenolic hydroxyl. This means that it is possible to obtain a titration curve with four jumps during the titration of a mixture of picric acid, dinitrophenol, mononitrophenol, and phenol.

Titration in nonaqueous media makes it possible to establish the presence of all the components in a mixture. Thus, during titration of a five component mixture consisting of perchloric acid, hydrochloric acid, trichloroacetic acid, acetic acid, and β-naphthol, a titration curve is obtained with five potential jumps. During titration of a mixture of the five acids, perchloric acid, nitric acid, oxalic acid, benzoic acid, and phenol, a curve is obtained with six potential jumps corresponding to the four monobasic acids and to the two neutralization steps of the dibasic oxalic acid.

Accordingly, titration of a mixture of acids in a differentiating solvent medium enables one to obtain curves with several potential jumps, so that it is possible to analyze multicomponent mixtures of acids.

The table contains results for the quantitative determination of individual benzoic acid derivatives and their mixtures. The titration curves of these compounds are shown in Fig. 5.

Several aliquots of each sample were analyzed. The determination was regarded as satisfactory when not less than three results coincided. As is evident from the table, individual acids and their mixtures can be determined with an accuracy of some tenths of a percent.

SUMMARY

A study has been made of the titration of derivatives of phenol, acetic and benzoic acids, as well as of mixtures of these compounds with organic and inorganic acids; the titrant was tetraethylammonium hydroxide in various organic solvents. It has been established that in a methyl ethyl ketone medium it is possible to titrate multicomponent mixtures consisting of three, four, and even five acids. The accuracy with which the acids mentioned can be titrated individually, or in their mixtures, is some tenths of a percent.

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THE EFFECT OF OXYGEN ADSORPTION ON THE OXIDATION OF FERROCYANIDE IONS ON A GOLD ELECTRODE

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The development of electroanalytical methods (coulometric titration, potentiometric and amperometric titrations during the passage of a current, etc.) requires a study of electrode reaction mechanisms under various conditions. The mechanism of an electrode reaction often depends on changes in the surface properties of the electrode used, on switching over from the pure metal to metal which has adsorbed hydrogen, oxygen, or various ions from solution. Adsorption is of particular importance for solid electrodes (platinum, gold, etc.) which are used in the region of positive potentials within which mercury dissolves, and are used for the analytical determination of systems with electrochemical properties similar to those of the system Hg, Hg^{n+}.

The platinum electrode is the most commonly used electrode in analytical chemistry; the gold electrode, however, has a number of advantages over the platinum electrode, the main advantage being its considerably wider useful potential range; for gold this is approximately 0.0-1.0 v relative to the normal hydrogen electrode (N.H.E.) in $HClO_4$ [1] from which oxygen has been removed, while for platinum this range is limited to 0.4-0.8 v [2]. The main reason for this difference is that on a gold electrode, the amount of hydrogen adsorbed is extremely low, while the adsorption potential for oxygen is high, as compared with a platinum electrode. It has been shown in the case of a platinum electrode [3] that adsorption of oxygen on the electrode leads to an essential change in the rate of the oxidation–reduction reactions, and, accordingly, leads to distortion of the polarization curves. The characteristics of the mechanisms of oxidation–reduction reactions have been studied to a considerably lesser extent on gold than on platinum electrodes.

In this connection therefore we thought that it would be expedient to study the effect of oxygen adsorption on a gold electrode during the course of some typical oxidation–reduction reaction which is of analytical interest. A suitable system for this purpose is the ferrocyanide–ferricyanide system.

It is known from published data that oxidation of ferrocyanide ions on a gold electrode [4-6] may be accompanied by polarization to varying extents. It has also been pointed out that the reaction rate drops when the gold is oxidized [7].

The work described here was devoted to a quantitative study of the rate of oxidation of ferrocyanide ions on a gold electrode as a function of the degree of passivity of the electrode in perchloric acid solutions.

The electrochemical properties of a gold electrode in pure perchloric acid solutions should be similar to those of the electrode in sulfuric acid solutions. The following published information is available on such properties in sulfuric acid solutions. During anodic polarization, it has been observed in a number of papers [8-11] that there is only one potential delay at 1.3-1.4 v, which is explained by the formation of a unimolecular film

of Au_2O_3, and one cathodic delay at 1.0-1.1 v corresponding to the reduction of surface oxide. Spectrographically pure gold whose surface is originally pure, and less pure gold containing 0.05% of impurities, behave similarly with respect to their electrochemical properties [11]. Will and Knorr [2], during a study of the passivity of a smooth gold electrode, used a method which they have suggested [12] of taking rapid anodic and cathodic polarization curves without turning off the current. On taking polarization curves for gold in 8 N H_2SO_4, the rate at which the potential changed being 1 v/ sec, they found that adsorption of oxygen starts at 1.37 v, oxygen being removed up to 0.85 v; the maximum amount of oxygen is removed at 1.1 v. In other papers [13, 14] other delays have been observed on the anodic curve; these can be ascribed to the presence of impurities in the metal [11]. Thus, the potential delay observed [15] at 0.76-0.85 v is related [11] to the presence of accidental contamination by iron. Nevertheless, it can be assumed that oxidation of gold on its surface does not only occur at potentials of 1.3-1.4 v. In fact, the amount of electricity consumed during anodic polarization of gold up to 1.2 v is approximately 50 μ coul/ cm^2 per 0.1 v [11], which is considerably in excess of the amount of electricity necessary for changing the double layer (10 μ coul/ cm^2 per 0.1 v for the positively charged surface of the solid electrode). The excess electricity is, obviously, used up on the adsorption of the fraction of the oxygen in the monolayer at potentials below 1.2-1.3 v, while at more positive potentials, monolayers and polylayers of oxygen are formed on the gold [9, 15].

Baumann and Shain [1] have taken polarization curves on a rotating gold electrode in the form of a wire, using perchloric acid of varying concentrations; the rate at which the potential was applied was varied while the electrode was subjected to different treatments. On the basis of their results [1], in 1 N $HClO_4$, and when the rate of change of potential is 3.7 mv/ sec, oxidation of gold starts at 1.3-1.4 v relative to the normal hydrogen electrode; only the main part of the oxygen is removed at 1.1 v, the remainder being removed at less positive potentials.

From an analysis of the work outlined above, it can be concluded that adsorption and desorption of oxygen on gold, as a rule, occur with appreciable overvoltage; the oxygen is removed at potentials which are 0.2-0.3 v less positive than those at which it is adsorbed. Up to 1.3 v relative to the normal hydrogen electrode, oxygen is adsorbed in amounts which are considerably less than those found in the monolayer, while it is removed below 1.1 v.

Method. The oxidation kinetics of ferrocyanide ions were studied in 1 N and 10^{-3}N $HClO_4$. The acid was twice distilled. The $K_4Fe(CN)_6 \cdot 3H_2O$ was recrystallized twice from twice-distilled water.

The work was carried out on a smooth gold disc electrode with a surface area of 0.058 cm^2; it was rotated at a speed of 3000 rpm. A platinized platinum electrode immersed in the same solution served as the second electrode. Polarographic curves were taken with a Heyrovsky polarograph. During the time the curves were being taken, the potential of the gold electrode was measured by a compensation method relative to the hydrogen electrode in a perchloric acid solution of the appropriate concentration. The experiments were made at a temperature of 25 ± 0.1 °C. in an atmosphere of purified nitrogen [3].

Prior to taking the curves, the gold electrode was usually kept at a potential of φ = 1.5 v, and then at φ = 0.5 v relative to the normal hydrogen electrode. The curves were taken from 0.2 v to the chosen value (1.0-1.9 v) and then back again. In some of the experiments the apparatus was momentarily switched from forward into reverse, while in some of these experiments the electrode was kept at the chosen potential value for 15 min and the reverse curve then taken. The rate of potential change was 400 mv/min.

EXPERIMENTAL

Typical polarographic curves for the oxidation of ferrocyanide ions on a gold electrode in 1 N $HClO_4$ are shown in Fig. 1. The ferrocyanide ion concentration was $3\text{-}4 \cdot 10^{-4}$M. Curve 1 in Fig. 1 was taken from 0.2 to 1.9 v, and the reverse curve 1' taken immediately. Curve 2' is the reverse curve obtained after the potential had been kept stable at 1.90 v for 15 min, while curve 3' is the reverse curve for the oxidation of ferrocyanide ions after the potential had been kept constant at 1.60 v. Curve 4 was taken in pure 1 N $HClO_4$, while curve 4' is the corresponding reverse curve obtained after keeping the potential stable in 1 N $HClO_4$ at 1.9 v.

Similar oxidation curves for the ferrocyanide ions were obtained in 10^{-3}N $HClO_4$.

The polarograms taken in the pure acid were found to be independent of the changes in the rate at which the electrode was rotated, in both 10^{-3}N and in 1 N $HClO_4$.

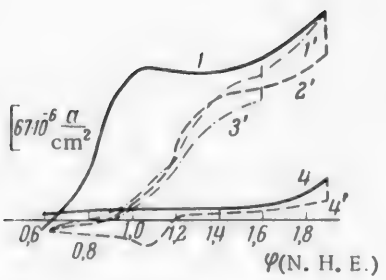

Fig. 1. Polarograms for the oxidation of ferrocyanide ions on a smooth gold electrode in 1 N $HClO_4$. Curve 1 was taken from less positive to more positive values. Curve 1' is the corresponding reverse curve. Curve 2' and 3' are the reverse curves obtained after keeping the potential stable at 1.90 v (Curve 2') and 1.60 v (Curve 3'). Curves 4 and 4' are the forward and reverse curves for 1 N $HClO_4$, in which the potential was stablized at 1.90 v.

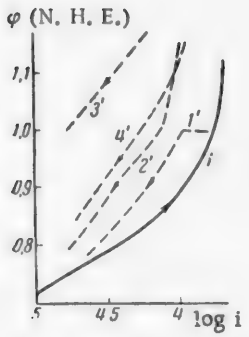

Fig. 2. Polarization curves for the oxidation of ferrocyanide ions on an unoxidized gold electrode (Curve 1) and on oxidized gold electrodes (Curves 1', 2', 3', and 4'). The reverse curves (dotted lines) were taken after the electrode potential had been kept constant at 1.00 v (Curve 1'), 1.30 v (Curve 2'), 1.60 v(Curve 3'), and 1.90 v (Curve 4').

In Fig. 2, the experimental results obtained on the oxidation of ferrocyanide ions in 1 N $HClO_4$ are expressed as a relation between the logarithm of the current density (log i) and electrode potential (φ). The curves are given after deduction of the current value in pure perchloric acid. The reverse curves (1', 2', 3', and 4') given in Fig. 2 were taken after the potential had been kept constant (stabilized) for 15 min at 1.00, 1.30, 1.60, and 1.90 respectively. From the curves shown in Figs. 1 and 2 it is quite clear that the oxidation current is appreciably less when the reverse curves are taken. The slope of the reverse curves in the current density range considerably lower than the limiting range, is 2-3 times greater. Similar curves were obtained in 10^{-3}N $HClO_4$, and also on instantaneous switching from the forward to reverse directions; in the latter case, however, the current drop becomes appreciable when the switching is carried out at 1.30 v, but not at 1.00 v.

On the ordinate in Fig. 3 is shown the observed decrease in the oxidation current of ferrocyanide ions ($\Delta \log i = \log i - \log i'$, where i is the current density in the forward direction, and i' is the current density in the reverse direction) as a function of the potential of the polarized electrode when the potential was kept constant at different values for 15 min in 1 N $HClO_4$. It is clear from these results that the slowing down of the reaction increases on increasing the intermediate polarization potential (the value at which the potential is kept constant) from 1.00 to 1.60 v, at which it has slowed down by an order of one and a half; keeping the potential constant at 1.90 v again leads to an increase in the reaction rate; it does not, however, reach the rate of oxidation of ferrocyanide ions in the forward direction. The reaction is slowed down to its maximum extent at 0.90 v, the slowing down then decreases as the region of the limiting diffusion current is reached, within which the rate is not determined by overvoltage.

Similar curves for the oxidation of ferrocyanide ions were obtained in 10^{-3}N $HClO_4$. For the curves shown in Fig. 4, preliminary activation of the electrode was carried out at 0.52 and 1.52 v relative to the normal hydorgen electrode. Similar results were also obtained when preliminary activation of the electrode was carried out at 0.32 and 1.32 v relative to the normal hydrogen electrode. Maximum slowing down of the reaction was observed in both cases at 0.6 v. When the decrease in current observed at this potential is expressed as a function of the values at which the potential was kept constant, Curve 1, Fig. 5, is obtained, corresponding to the results in Fig. 4. Curve 2, Fig. 5, was obtained from the experiments in which activation was carried out at 0.32 and

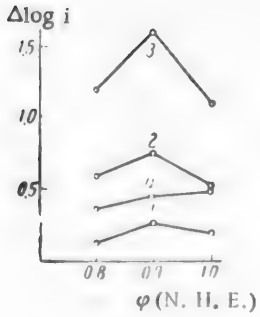

Fig. 3. Curves showing the relationship between the extent to which the oxidation of ferrocyanide ions is slowed down and the electrode potential in 1 N $HClO_4$; the potential is kept constant at the following values: 1.00 v (Curve 1); 1.30 v (Curve 2); 1.60 v (Curve 3); 1.90 v (Curve 4).

1.32 v. A comparison of curves 1 and 2, Fig. 5, shows that the decrease in current, and the value of the constant potential (the value at which the potential is kept constant) which gives rise to the greatest current drop, depend only to a small extent on the activation potential used for the preliminary treatment of the electrode. The reaction is slowed down to its greatest extent when the potential is kept constant at 1.0-1.3 v. The activation potentials used for the preliminary treatment of the electrode only appreciably affect the extent to which the reaction is slowed down when the potential is kept constant at values higher than 1.30 v.

Curve 3, Fig. 5, which shows the extent to which the reaction is slowed at 0.9 v, is a similar curve for the oxidation of ferrocyanide ions in 1 N $HClO_4$. The maximum decrease in the current is observed when the potential is kept constant at 1.60 v. The current drop in 1 N $HClO_4$ is half of an order higher than in 10^{-3}N $HClO_4$.

In our opinion the drop in the oxidation current of ferrocyanide ions is explained by adsorptive passivation of the gold electrode. Adsorption of oxygen, which leads to the greatest slowing down effect, occurs in the potential range above 1.00 v relative to the normal hydrogen electrode, while removal of the adsorbed oxygen occurs at potentials which are appreciably less positive; i.e., adsorption and desorption occur with overvoltage, which leads to hysteresis on the oxidation curves for gold taken in the forward and reverse directions. A similar hysteresis effect has been observed during the oxidation of divalent iron on gold and platinum [1, 3]. Slowing down increases as the amount of adsorbed oxygen accumulates or during the aging of the adsorbed layer (an effect caused by keeping the potential constant for some time). What was unexpected was that the slowing down only increases up to a certain value of the stabilized potential (the value at which the potential is kept constant); when the latter is increased further, the slowing down decreases. This phenomenon has not been observed during the oxidation of iron on a platinum electrode [3], although the slowing down has been observed to decrease even in this case on increasing the adsorption potential of oxygen on the platinum from 1.2 to 1.4 v. Such a form of the relationship between the slowing down and the value of the stabilized potential may be explained on the assumption that it is the adsorbed oxygen which exhibits this slowing down effect, while the layer of phase oxide does not exhibit an appreciable slowing down effect.

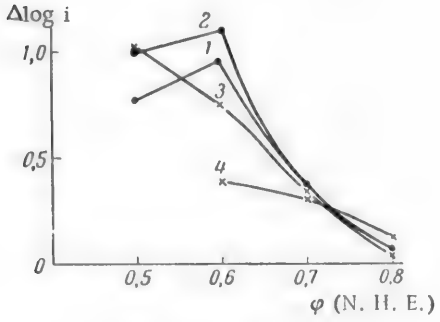

Fig. 4. Curves showing the relationship between the extent to which the oxidation of ferrocyanide ions is slowed down and the electrode potential in 10^{-3}N $HClO_4$, when the potentials were kept constant at the following values: 1.02 v (Curve 1); 1.32 v (Curve 2); 1.62 v (Curve 3); and 1.92 v (Curve 4).

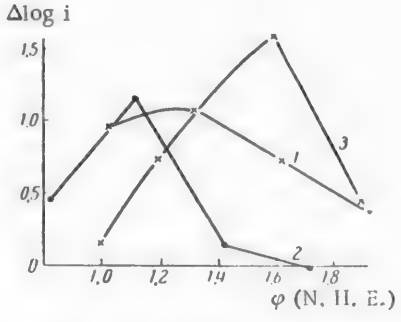

Fig. 5. Curves showing the relationship between the extent to which the oxidation of ferrocyanide ions is slowed down and the values at which the electrode potential is kept constant, for the following potentials of the polarographic curve: 0.60 v (Curves 1 and 2, 10^{-3}N $HClO_4$); and 0.90 v (Curve 3, 1 N $HClO_4$).

The difference between the stabilized potentials which give the maximum current drop in 1 N $HClO_4$ and in 10^{-3}N $HClO_4$, and which is equal to 0.30-0.50 v, has the same sign as the difference (0.18 v) in the adsorption potentials of oxygen on gold at pH values of 3 and 0 [10]; nevertheless, it is greater than the latter. This, presumably, can be explained by differences in the structure of the adsorbed layer at the different pH values.

A sharp decrease in the current strength at a potential of about 1.50 v relative to the normal hydrogen electrode (see [16]), has been observed in some cases on a platinum electrode during the oxidation of ferrocyanide ions in 0.1 N H_2SO_4; hysteresis of the curves similar to that described has also been observed when these curves were taken from less positive to more positive potentials, and in the reverse direction (see [3]). The results of these experiments also can be explained by passivation of the electrode during adsorption of oxygen on it, and removal of oxygen occurring with overvoltage. Nevertheless, in order to get reproducible results with a platinum anode it is necessary to be much more strict in observing the conditions than in the case of a gold electrode; the conditions used for preliminary activation of the electrode must be kept the same, as well as the initial and final potentials of the oxidation curve. This fact is one reason in favor of the use of a gold electrode as an anode in analytical chemistry.

Nevertheless, even when a gold electrode is used in the potential region within which gold is oxidized, it is necessary to take into account the influence of the passivizing action of oxygen on the course of the oxidation–reduction reactions.

It follows from our results that the potential range within which the gold electrode can be used for automatic polarographic determination of ions can be extended in some cases to 1.5-1.6 v in the positive direction. Under these conditions, it is essential to use either curves taken from less positive potentials to more positive potentials, or to use the reverse curves when the electrode reaction is only slowed down to a relatively small extent by the adsorption of oxygen on the gold electrode.

In cases of intermittent changes in the current or potential of the gold electrode within the potential range where adsorption of oxygen occurs, it is necessary to activate the electrode before measuring each point, by switching anodic and cathodic polarizations, and to take a reading after definite time intervals from the start of electrolysis.

I should like to thank A. N. Frumkin and B. N. Kabanov for taking part in the discussion of results.

SUMMARY

Anodic oxidation of ferrocyanide ions in 1 N and 10^{-3}N $HClO_4$ has been studied polarographically on a rotating gold electrode.

Adsorption of oxygen on gold decreases the rate of oxidation of ferrocyanide ions by an order of 1-1.5.

The reaction of the ferrocyanide ion is slowed down to a greater extent in 1 N $HClO_4$ than in 10^{-3}N $HClO_4$.

Slowing down of the oxidation of ferrocyanide ions increases on increasing the potential at which oxygen is adsorbed to a definite value of 1.60 v in 1 N $HClO_4$ and 1.1-1.3 v in 10^{-3}N $HClO_4$; the slowing down thereafter decreases.

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A STUDY OF THORON AND ITS REACTIONS WITH SEXIVALENT URANIUM

V. A. Mikhailov

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Organic reagents containing the o-arsono-o-hydroxyazo group have been recommended by Kuznetsov [1-3], and are finding ever increasing use in analysis. Thus, thoron has been used for the determination of thorium [4-9], zirconium [10], quadrivalent uranium [11], quadrivalent plutonium [12], beryllium [13], and lithium [14]; arsenazo has been used for the determination of sexivalent uranium [15], the rate earths [16], zirconium [17], aluminum [18], and other elements. Of considerable interest in this connection is the study of the properties of these reagents and of the compounds which they form, establishment of the effect of pH, and clarification of the reaction mechanism. Work along these lines has appeared in recent years, and thoron [19-21], arsenazo [22], and their compounds [6, 11-14, 21, 23, 24] have been examined. One drawback of some of these papers is that the pH of the media have only been examined over comparatively narrow ranges. As a consequence the experimental results are not treated accurately.

1. The Behavior of Thoron at Various pH Values

Thoron has been examined spectrophotomerically earlier by Adamovich and Didenko at pH 1.4-12.6 [19], Margenum at pH 5-13.5 [20], and Byrd [21]. In the work described here spectrophotometric studies were carried out within the pH range -1 to 15. They were supplemented by electrophoretic results.

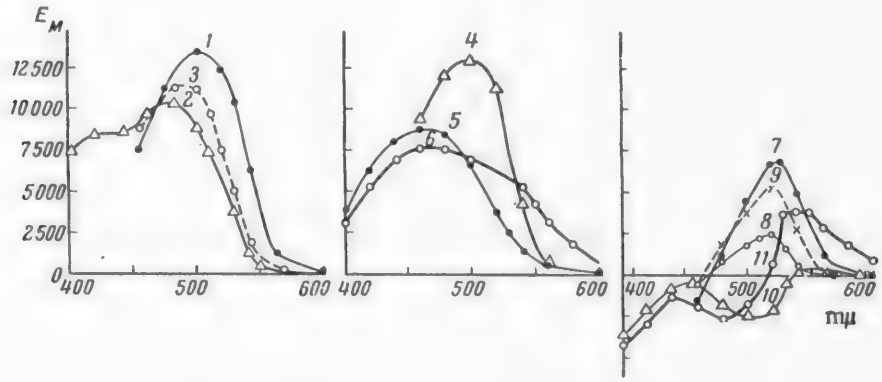


Fig. 1. Absorption curves for thoron at various pH values. Reference solution, water. 1) pH 1; 2) pH 0-3; 3) pH 5-7; 4) pH 9-10; 5) pH 12-13; 6) pH 15. Reference solution, thoron solution at pH 1; 7) pH 1; 8) pH 5-7; 9) pH 9-10; 10) pH 12;13; 11) pH 15.

A 0.2% aqueous solution of commercial thoron was prepared; the commercial material contains 78% of 1-(2-arsonobenzolazo)-2-hydroxynaphthalene-3,6-disulfonic acid. The amount of the principal component of the material was determined in two ways: 1) by drying at 150°, and calcining at 1100°, the amount of water and nonvolatile impurities were determined; 2) by spectrophotometric titration of thoron with a thorium salt in 0.1 M acid; thoron and thorium interact in the ratio of 2 : 1 [4]. The optical density was measured on a SF-4 spectrophotometer using glass cuvettes with layer thicknesses of 1.0 and 2.0 cm. The thoron concentration was 1.2×10^{-4} M.

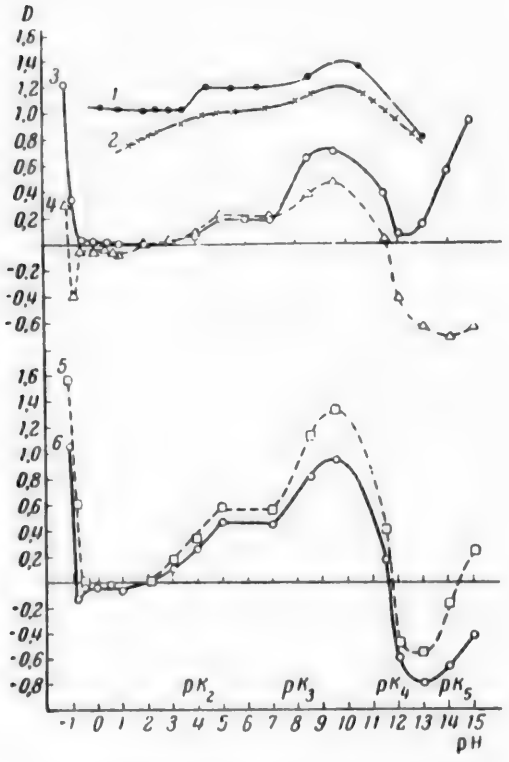
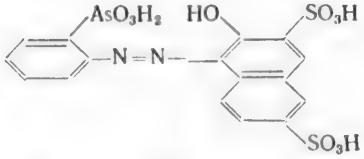


Fig. 2. Effect of pH on the light absorption of thoron solutions. 1) Thoron 1.2×10^{-4}M, cuvette 1.0 cm, λ = 500 mμ, reference solution-water; 2) Adamovich and Didenko's results [19], λ =490 mμ; 3-6) thoron 1.2×10^{-4}M, cuvette 2.0 cm, reference solution-thoron solution at pH 1; 3) λ = 540 mμ; 4) λ = 480; 5) λ = 520; 6) λ = 500 mμ.

The color of thoron solutions depends on the pH; in concentrated hydrochloric acid the color is raspberry, while in dilute acid it is orange, and in a weakly alkaline (ammoniacal buffer solution) medium it is reddish; in dilute alkaline solutions it is yellow, and in concentrated alkaline solutions raspberry. These color changes of the solutions are reversible. The absorption curves of thoron solutions at some of the most characteristic pH values: -1, 0-2, 5-7, 9-10, 12-13, and 15 are given in Fig. 1. The optical density was measured with respect to a solution of thoron at pH 1, and also with respect to water. The latter curves were obtained from the former by adding the absorption of the reference solution to them.

As is evident from Fig. 2, which expresses the relationship between the light absorption of thoron solutions at various wavelengths and pH, the curves in Fig. 1 belong to various states of thoron. A characteristic feature of these states is the horizontal sections at the extremes or ends of the curves in Fig. 2. It can be assumed, as other authors have done [19-22], that these states are various stages in the dissociation of thoron. The maximum values of the light absorption and the molar coefficients for the various forms of thoron are given in Table 1.

From the formula of thoron H_5T:



it is clear that five stages of acid dissociation are possible for thoron, i. e. six different forms: H_5T, H_4T^-, H_3T^{2-}, H_2T^{3-}, HT^{4-} and T^{5-}. Moreover, because of the presence of nitrogen atoms in the molecule, addition of H^+ ions to give a seventh (onium)form is possible: H_6T^+. From Figs. 1 and 2, according to the spectrophotometric results at various pH's, only six different forms of thoron can be distinguished, while only five at the best can be distinguished visually.

In order to avoid possible arbitrariness in interpreting the curves in Fig. 2, electrochromatographic experiments were carried out on the transport of the various forms of thoron [25]. A few drops of thoron solution at a given pH was placed on the middle of a sheet of filter paper 30 cm long and 1-2 cm wide. The remainder of

TABLE 1

Maximum Light Absorption of Thoron at Different pH Values

pH	Reference solution–water			Reference solution – thoron at pH 1		
	λ_{max} mμ	$E\lambda$ max	EE_{490}, according to [19]	λ_{max} mμ	$E\lambda$ max	E_{440}
—1	510	14 000	—	530	7000	5000
0—3	480	11 000	7300	—	—	—
5—7	490	13 000	9800	520	2500	600
9—10	490	14 000	11 400	520	5000	3000
12—13	460	9 000	—	560	450	250
15	470	8 000	—	540	4000	4000

TABLE 2

Electrochromatographic Behavior of Thoron

Medium	Movement of thoron	
	direction	rate cm/min 10^5
pH-1(11 M HCl)	Toward the cathode	-50 ± 10
pH-0.8(6 M HCl)	Toward the anode	+50 ± 10
pH 1(0.1 M HCl)	" "	+25 ± 15
pH 5(acetate buffer solution)	" "	+17 ± 3

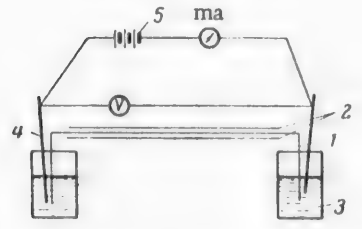


Fig. 3. Schematic diagram of the apparatus used for electrochromatography. 1) Sheet of filter paper; 2) glass plates; 3) beakers containing the solutions; 4) carbon electrodes; 5) dc source.

the sheet was moistened with a solution of the same pH. The paper was placed between two glass plates, while the ends of the paper were placed in beakers containing buffer solutions. Carbon electrodes were immersed in these beakers and a dc current at a voltage of 100-400 v (Fig. 3) passed through them for 0.5-1 hr.

From the results obtained (Table 2) it is clear that in a medium with a pH of -1, thoron is positively charged, while in media with pH higher than -0.8 it is negatively charged. Accordingly, in concentrated hydrochloric acid the form H_6T^+ is present, while at pH 0 to 3 presumably H_4T^- is present. Next, it is obvious that at pH 5-7 H_3T^{2-} predominates, while at pH 9-10, H_2T^{3-} is the main component, at pH 12-13, HT^{4-}, and at pH 15, T^{5-}. These observations, therefore, do not confirm the assumptions made by other authors [19-21] that the predominating thoron form at pH 1-2 is H_3T^{2-}. In each case the treatment adopted by other authors agrees to a lesser extent with the curves in Fig. 2 than the results given here.

An approximate evaluation of the successive dissociation constants of thoron by means of the equation:

$$H_nT^{(5-n)-} \rightleftarrows H_{n-1}T^{(6-n)-} + H^+$$

can be carried out with the aid of the curves in Fig. 2. As noted above the horizontal parts, and also the extremes and the ends of the curves, can be regarded as regions in which the respective forms of thoron predominantly exist. In the intermediate regions, points at which 50% dissociation occurs can be found. At these points the light absorption has an intermediate value between the extreme values, and the concentrations of $H_nT^{(5-n)-}$ and $H_{n-1}T^{(6-n)-}$ are equal. From the expression for the dissociation constant:

$$K = \frac{[H_{n-s}T^{(6-n)-}\ H^+]}{[H_nT^{(5-n)-}]}$$

it is clear that K is numerically equal to $[H^+]$, and $pK = (pH)_{50\%}$. These pK values are given in Fig. 2 and in

TABLE 3

Indices of the Dissociation Constants of Thoron

Dissociation scheme	The groups in thoron which participate in the reaction	According to Fig. 2	According to published results [19] 1*	[19] 2*	[20] 1*	[20] 2*	[21] 1*	[21] 2*
$H_6T^+ \rightleftarrows H_4T^- + 2H^+$ $p(K_{base} \cdot K_1)$	$\geqslant NH^+$ и $-SO_3H$	~2**	—	—	—	—	—	—
$H_4T^- \rightleftarrows H_3T^{2-} + H^+$ pK_2	$-SO_3H$	~4	—	2,3?	—	3,7	—	3,36
$H_3T^{2-} \rightleftarrows H_2T^{3-} + H^+$ pK_3	$-AsO(OH)_2$	~8	2,3	5,8?	3,7	8,4	3,36	7,92
$H_2T^{3-} \rightleftarrows HT^{4-} + H^+$ pK_4	$-AsO_2OH^-$	~11,5	5,8	11,7	8,4	11,8	7,92	—
$HT^{4-} \rightleftarrows T^{5-} + H^+$ pK_5	$-OH$	~14	11,7	—	11,8	—	—	—

* pK according to the authors of the papers cited; 2) pK values on the basis of the present work.

** $p(K_{base} \cdot K_1) = 2(pH)_{50\%}$

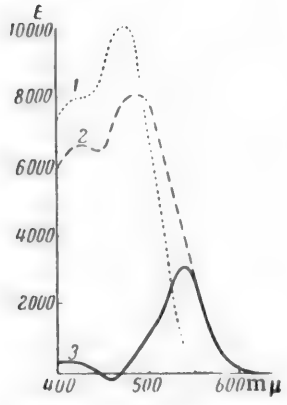


Fig. 4. Light absorption curves of the solutions: 1) Thoron in 0,1 M HCl, reference solution-water; 2) compound of sexivalent uranium with thoron at pH 4 (urotropine buffer solution). Measurement carried out relative to water; 3) compound of uranium with thoron at pH 4, relative to thoron solution.

Table 3. In Table 3 is given the most probable interpretation of the successive dissociation constants of thoron, as determined in the work described here, and derived on the basis of other results. The values quoted by other authors are included for comparison [19-21].

As is evident from Table 3, it is only possible here to give an evaluation of the product of the basicity constant ($K_{bas.}$) and the first acid dissociation constant of thoron (K_1): $K_{bas} \cdot K_1 = 10^2$. On the basis of the results given, it is not possible to give an evaluation of their separate values. Such an evaluation is possible for the remaining acid dissociation constants of thoron.

On the basis of the number of forms of thoron which have been determined in the present work, and the indices of its successive dissociation constants, it is suggested that the pK values proposed by other authors—interpreted by these authors as the first pK's of the dissociation of the arsonic group—are in fact shifted by one degree and are the pK's for the dissociation of the second sulfonate group. It follows from Table 3 that if this is the case, the results of Byrd [21] and Margenum [20] agree with the values found in the present work. The first two constants calculated by Adamovich and Didenko [19] differ by two degrees, while the third also agrees with the value established in the present work. The dissociation constants given here are concentration constants and refer to solutions containing 0,1-1 M salt.

2. The Interaction of Sexivalent Uranium and Thoron

As pointed out by Kuznetsov [1, 2], sexivalent uranium interacts with thoron in an acetic acid medium to give raspberry color. He established that 2 mg of uranium does not interfere with the determination of thorium in 0,3 M hydrochloric acid. Thomason et al [4] have pointed out variations in the influence of uranium during the determination of thorium, when the pH of the solutions is varied from 0,4 to 1,25.

TABLE 4

Electrochromatography of the Compound of Sexivalent Uranium with Thoron

Expt. No.	Medium	Concentration, M		Displacement of spot center		
		uranium	thoron	material	direction	rate, cm/min
1	pH 2 0,01 *M* HCl	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	Thoron	to anode	$+7 \cdot 10^{-5}$
				Uranium thoronate	—	$<0,3 \cdot 10^{-5}$
				Thoron	to cathode	$-7 \cdot 10^{-5}$
2	pH 2 0,01 *M* HCl	$4 \cdot 10^{-4}$	$20 \cdot 10^{-4}$	Thoron	to anode	$+13 \cdot 10^{-5}$
				Uranium thoronate	—	$<0,3 \cdot 10^{-5}$
3	pH 4 Urotropine buffer solution	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	Uranium thoronate	—	$<0,3 \cdot 10^{-5}$
4	pH 8 Ammoniacal buffer solution	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	Uranium thoronate	to anode	$+9 \cdot 10^{-5}$

Note. Experiments 1-3 lasted one hr; while experiment 4 took half an hour; voltage 500 v.

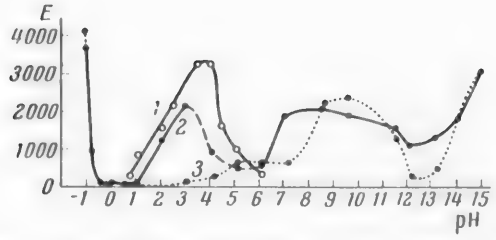


Fig. 5. Effect of pH on the light absorption of thoron and its compound with sexivalent uranium. 1) Uranium 10^{-3} M, thoron 1.8×10^{-4} M; urotropine buffer pH 1-6, λ = 545 mμ; 2) uranium 4×10^{-4} M, thoron 3×10^{-4} M, acetate buffer pH 3-6, λ = 545 mμ; 3) thoron solution, λ = 540 mμ.

The absorption curves of thoron and of the compound which this reagent forms with sexivalent uranium are shown in Fig. 4. The biggest difference between thoron itself and its compound with uranium is observed at 545 mμ; this is similar to that observed for the compounds formed between thoron and quadrivalent cations [4, 6, 10-12]. All optical density measurements were subsequently carried out relative to a thoron solution with the same total concentration. Thus, in all cases, the color of the unreacted reagent was subtracted, while the optical density measured was determined by the light absorption of the compound of thoron with sexivalent uranium alone. Although the light absorption of the compound thereby decreases, it is still always proportional to the concentration of the compound, independently of the ratio of uranium to thoron taken.

The relationships between the light absorption of thoron and of its compound with uranium and the pH are compared in Fig. 5. The biggest difference in color between thoron and its uranium compound is observed at pH 4 (an urotropine buffer solution). In an acetate buffer, the color of the compound is significantly weaker. During visual observation the following color changes are observed: in concentrated acid, raspberry; in dilute acid, the orange color of the reagent; at pH 4, raspberry; at pH 6, yellow; at pH 8-9, red; at pH 12 yellow; and in concentrated alkali back again to the raspberry color of the sexivalent uranium compound.

Using the method of isomolar series (Fig. 6), it was established that uranium reacts with thoron in a molar ratio of 1 : 1. The molar light absorption coefficient of the compound of uranium with thoron at a wavelength of 545 mμ is 3200 (see Fig. 4), after subtracting the light absorption of thoron itself.

As noted already the reference solution used in all the measurements was a thoron solution with the same concentration. For calculating the points in Fig. 7 and the results in Table 4, the uranyl thoronate concentration was determined by means of the formula

$$[UO_2H_{4-x}T] = \frac{D_{545}}{E_{545} \cdot l} = \frac{D_{545}}{3200 \cdot l} .$$

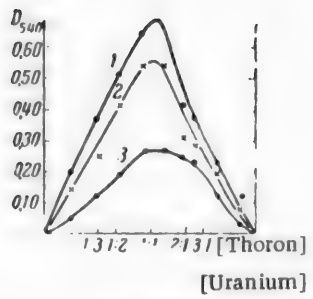


Fig. 6

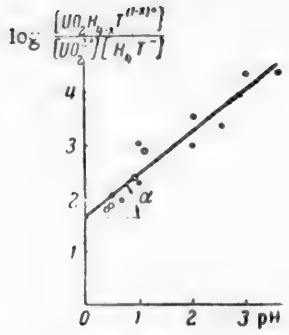


Fig. 7

Fig. 6. Composition of the uranium compound with uranium by the isomer series method. λ = 545 mμ. Cuvette 1.0 cm. 1) pH 4, uranium + thoron 8×10^{-5}M; 2) pH 4, uranium + thoron 6.5×10^{-5}M; 3) pH 2, uranium + thoron 6.5×10^{-5}M.

Fig. 7. The relation between log $\frac{[UO_2H_{4-x}T^{(1-x)+}]}{[UO_2^{2+}][H_4T^-]}$ and pH. •) points according to results of Thomason et al.[4]. The straight line was drawn by the method of least squares [27]: y = 1.6 + 0.8 pH, tangent α = 0.8 to about 1.

The uranyl and thoron concentrations were calculated by difference.

Presumably, uranium reacts with thoron according to the following scheme:

$$UO_2^{2+} + H_4T^- \rightleftarrows UO_2H_{4-x}T^{(1-x)+} + x \cdot H^+;$$

here H_4T^- is the thoron ion at pH 0-3, x is the number of ions in thoron replaced by uranium. Since the equilibrium constant of the reaction $K_{equilib.}$ is equal to:

$$K_{eq} = \frac{[UO_2H_{4-x}T^{(1-x)+}][H^+]^x}{[UO_2^{2+}][H_4T^-]},$$

then by taking logarithms and transforming this equation, we get

$$\lg \frac{[UO_2H_{4-x}T^{(1-x)+}]}{[UO_2^{2+}][H_4T^-]} = \lg K_{eq} + x \cdot pH$$

In Fig. 7 is given the straight line constructed on the basis of points on Curve 1, Fig. 5, and some other data, over the pH range 0.4-3.5. This straight line can be described by the last equation. The slope of the straight line in Fig. 7 permits the coefficient x to be determined. We find in this way that x is about 1. From this it follows that the interaction of sexivalent uranium with thoron is of the type:

$$UO_2^{2+} + H_4T^- \rightleftarrows UO_2H_3T + H^+$$

It follows from this scheme that the compound formed in weakly acid solutions is electrically neutral. To confirm this we carried out some electrochromatographic experiments on the uranium compound at various pH's. When the experiments were complete the uranium was located on the paper sheet by means of potassium ferrocyanide; transfer of thoron and the compounds was observed visually. The experimental results are given in Table 4. As is evident from experiments 1-3, the compound of uranium with thoron hardly migrates at all and appears to be electrically neutral, since the transport velocities in the electrical field of the reagent itself (experiments 1 and 2) and of the cation UO_2^{2+} (experiment 1 – low pH and insufficient thoron) are considerably greater (1-2 orders at least).

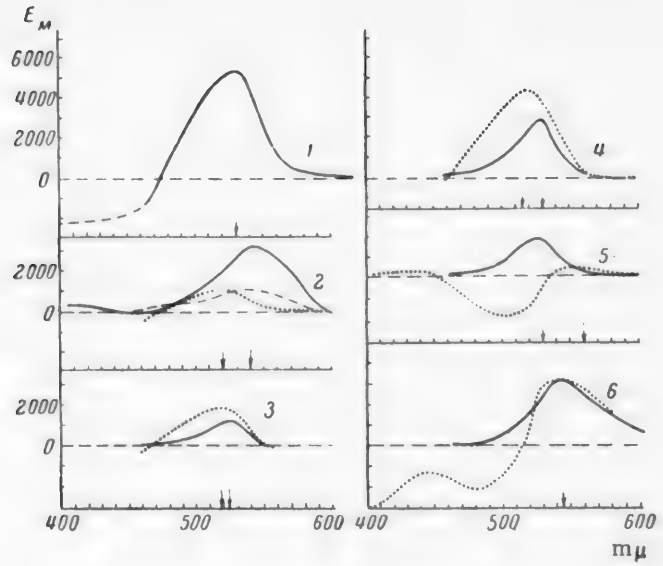


Fig. 8. Light absorption curves of thoron and of the compound of uranium with thoron at various pH's. 1) pH 1; 2) pH 4; 3) pH 6; 4) pH 9.5; 5) pH 12; 6) pH 15. ···· Thoron; —— uranium compound; --- the uranium compound in an acetate buffer solution.

During observations of solutions of sexivalent uranium and thoron at ratios greater than 1 : 4, it was observed that an orange precipitate is formed after 24 hr in media with pH from 2 to 6. In order to determine its composition, a solution with a pH of 4 was prepared (urotropine buffer solution) in which the concentrations of sexivalent uranium and thoron were 8×10^{-4} M and 4×10^{-4} M respectively. After removal of the precipitate on the next day, analysis of the decanted solution showed that the uranium concentration as found by the luminescent method was 3×10^{-4} M, while the uranium thoronate concentration was found to be 5×10^{-5} M by a spectrophotometric method. Consequently, the ratio of uranium to thoron in the precipitate is $5 \times 10^{-4} : 3.5 \times 10^{-4} =$ = 1.4 : 1 or about 1.5 : 1. Presumably, formation of the precipitate is connected with the formation of a sparingly soluble salt of sexivalent uranium thoronate with excess uranium, in which hydrogen ions are expelled from the sulfonate or arsono group.

The absorption curves of the various forms of thoron and of its compound with uranium at certain pH's are compared in Fig. 8. In strongly acid solutions the light absorption curves do not differ from each other, either in the presence or absence of uranium. Curves 1 and 2 in Fig. 5 show that at pH 1-3 formation of a compound between sexivalent uranium and thoron occurs. The weakening of the color at pH's between 4 and 6, as follows from Kuznetsov's hypotheses [26], is connected with a change in the state of the uranium bond in the compound, e. g.,with the phenol hydroxyl. In an acetate medium, however, over the same pH range, competitive formation of acetate complexes of uranium may occur (Curve 2, Fig. 5).

On increasing the pH further, the color changes for the compound of uranium with thoron are reminiscent of the corresponding changes for thoron itself (Curves 2 and 3, Fig. 5), although, as is evident from Fig. 8, the absorption curves of the solutions do not completely coincide at equal pH values. Formation of uranate precipitates was not observed even in strongly alkaline media. It is obvious that under such conditions soluble alkaline salts of uranium thoronate are formed. This is confirmed by the electrochromatography of the compounds at pH 8 (Table 4).

The assumption that the change in the color of the compound which occurs on increasing the pH above 4 is related to changes in the composition of the compound does not receive much support from the experimental results. Uranium and thoron were mixed together in approximately equimolar amounts, the following results therefore do not support such an assumption: when the compound was examined electrochromatographically in a solution with pH 8, only one band was observed for the compound (Table 4); no separate bands for uranium

TABLE 5

Calculation of the Formation Constants of the Compound Formed Between Sexivalent Uranium and Thoron

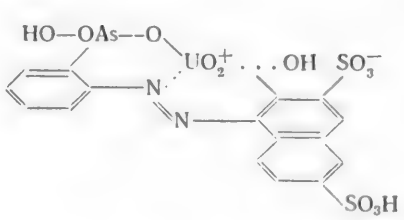
№	[H+] M	Taken, M x 10^4		D_{545}	Equilibrium concentrations, M x 10^4			K_{equil}
		uranium	thoron		UO_2^{2+}	UO_2H_3T	H_4T^-	
1	0,1	2,0	2,5	0,012	2,0	0,04	2,5	8
2	0,1	3,0	2,5	0,025	2,9	0,08	2,4	11
3	0,1	9,5	2,5	0,070	9,3	0,22	2,3	10
4	0,1	21	2,5	0,120	21	0,38	2,1	9
5	0,1	42	2,5	0,220	41	0,69	1,8	9
6	0,1	63	2,5	0,295	62	0,92	1,6	9
7	0,1	84	2,5	0,345	83	1,1	1,4	12
8	0,01	0,85	5,7	0,06	0,66	0,19	5,5	5
9	0,01	1,7	4,8	0,13	1,3	0,41	4,4	7
10	0,01	2,4	4,1	0,20	1,8	0,63	3,5	10
11	0,01	3,1	3,4	0,27	2,3	0,84	2,6	14
12	0,01	3,8	2,7	0,28	2,9	0,87	1,8	17
13	0,01	4,4	2,1	0,27	3,6	0,84	1,3	18
14	0,01	4,9	1,6	0,25	4,1	0,78	0,8	25
15	0,01	5,5	1,0	0,13	5,1	0,41	0,6	18
16	0,01	6,0	0,5	0,03	5,9	0,10	0,4	4
Mean (confidence level 0.95).								11±9

and thoron were observed. The absence of uranate precipitates in strongly alkaline solutions also testifies to the absence of any changes in composition.

The reaction constant for the formation of the compound of sexivalent uranium with thoron, according to the scheme advanced above, can be determined by means of Fig. 7. The intercept made by the straight line on the ordinate is numerically equal to the free term in the equation for the straight line: log $K_{equilib.}$ = 1.6 and $K_{equilib.}$ = 40. The constant of this reaction can also be calculated on the basis of the results of the other series of spectrophotometric measurements given in Table 5.

As is evident from the Table, the mean value of $K_{equilib.}$ is almost the same as that determined by means of Fig. 7. The constancy of $K_{equilib.}$, when determined on the basis of the results of different series of measurements, confirms the scheme advanced for the reaction leading to the formation of the compound of sexivalent uranium with thoron at pH 0.4-3.5. The general value is $K_{equilib.} = 25 \pm 15$.

If the treatment adopted above of explaning the changes in light absorption with changes in pH is true, then, according to Curve 2, Fig. 5, it should be possible,on the basis of the points corresponding to the pH for a 50% color, to evaluate the indices of the acid dissociation constants of uranium thoronate $H_3(UO_2T)$. The following structural formula can be advanced for it:



The indices of the acid dissociation constants were found to be approximately equal to: pK_1 about 6.5 (sulfonate group); pK_2 about 11.5 (arsono group), and pK_3 about 14 (phenolic hydroxyl). They can be compared with the respective indices for the thoron constants: pK_2 about 4, pK_3 about 8, pK_4 about 11.5, and pK_5 about 14. The

values of the last two constants coincide. Obviously, the state of the corresponding groups, i. e.,the state of one hydroxyl of the arsono group and of the phenolic hydroxyl in uranium thoronate differ very little from their states in thoron itself, when the pH is > 6.

Thus, the effect of pH on the color of the compound formed between sexivalent uranium and thoron at pH 0.4-3.5 is well described by the equation for its formation reaction (uranium: thoron = 1 : 1). At pH 4-6, presumably, there is a change in the state of the bond between uranium and thoron, while at higher pH's,acid dissociation of the compound occurs. At a pH of about 4,excess uranium forms a sparingly soluble compound (uranium : thoron = 1.5 : 1) with uranium thoronate.

It should be pointed out that although the work described here does supplement existing information on the interaction of cations with o-arsono-o'-hydroxyazo compounds, the problem of the nature of the bonds between uranyl—and other cations—and the arsono and azo groups, and the problem of the changes with occur on increasing the pH, still remain to be solved. Ideas which have already been published [26] are only in partial agreement with the results given here.

SUMMARY

A study has been made of the behavior of thoron and of its compound with sexivalent uranium when the pH of the solution is changed from -1 to 15.

Six forms of thoron have been identified by a spectrophotometric method. It has been shown by means of electrochromatography that thoron is positively charged in concentrated acid, while at pH $\geq$ 0 it is negatively charged. The values of the successive dissociation constants of thoron have been established: $pK_2 \sim 4$, $pK_3 \sim 8$, $pK_4 \sim 11.5$, $pK_5 \sim 14$.

Formation of compound between sexivalent uranium and thoron starts at pH 0.4. The maximum color is observed at pH 4. Uranium reacts with thoron in the molar ratio of 1 : 1, one atom of hydrogen being thereby displaced. This compound has been shown to be electrically neutral by electrochromatography. The reaction constant of its formation at pH 0.4-3.5 is 25 ± 15. The values of the acid dissociation constants of uranium thoronate have been established at pH > 6: $pK_1 \sim 6.5$, $pK_2 \sim 11.5$, $pK_3 \sim 14$.

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 17. 8,8'-DIQUINOLYLDISULFIDE- A NEW SELECTIVE REAGENT FOR THE PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF COPPER*

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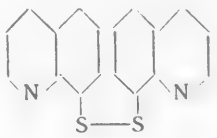
Despite the large number of methods already published for the determination of copper, determination of small amounts of this element is still one of the pressing problems of analytical chemistry. Apart from its marked tendency to form complexes, copper can also be readily converted into its univalent from which has strong reducing properties. The reducing properties of cuprous ions can be used for the analytical determination of copper, particularly when the reagent produced during the reduction forms (during the second phase of the reaction) an intensely colored or a sparingly soluble compound with copper.

A reagent which answers these requirements is 8,8'-diquinolyldisulfide (subsequently referred to as disulfide) which is obtained by the oxidation of 8-mercaptoquinoline**



We have established previously that cuprous ions reduce disulfide to 8-mercaptoquinoline, copper 8-mercaptoquinolinate with the structure indicated in [1] being subsequently formed.

A very selective method for the detection of copper on the basis of the formation of the complex mentioned above has been described previously [2]. The highly selective method described here for the quantitative determination of copper can be regarded as belonging to the class of so-called "in situ nascendi" reagent methods [3], and has the advantage that the 8-mercaptoquinoline which is formed during the reaction reacts with copper in strictly equivalent amounts. This also accounts for the high selectivity of the method suggested; as we have shown [4], the selectivity is incomparably less if excess thiooxine (8-mercaptoquinoline) is used, even in presence of powerful masking agents.

* For Communication 16, see Izvestiya Akad. Nauk Latv. SSR, No. 1, 97 (1960).

** For the synthesis of 8-mercaptoquinoline and 8,8'-diquinolyldisulfide see Bankovskii, Ievin'sh, and Luksha [5].

Masking agents (usually tartrates) have to be used in the new method, mainly in cases where it is necessary to keep in solution those metal salts (Sb, Bi , Ti, Fe, Cr, etc) which readily hydrolyze in very weak acid or alkaline media.

Extractability of the Copper Complex as a Function of the pH of the Medium and the Nature of the Reducing Agent

A 0.2% solution of disulfide in chloroform, which is, at the same time, the best extractant for copper 8-mercaptoquinolinate, was used in all the experiments described below. When a 0.2% chloroform solution of disulfide was used, only a small amount of it was consumed—lost to the aqueous phase; it was found, however, that when a lower concentration was used, the copper was not completely extracted. The pH range for the extraction of the copper complex was determined when ascorbic acid and hydroxylamine hydrochloride were used as the reducing agents; the pH range was also determined in the absence of reducing agents, using the theoretical amount of thiooxine (the sodium salt $C_9H_6NSNa \cdot 3H_2O$ [5] was used). In order to keep the conditions constant, and to eliminate secondary factors as far as possible, the volume of the aqueous phase was kept at 50 ml both in these experiments and in all subsequent experiments. To 40 ml of buffer solution with a known pH, and contained in a separating funnel (150 ml) was added a solution (5 ml) containing 50 μg of copper; 5 ml of the reducing solution (a 20% ascorbic acid solution of a 50% hydroxylamine hydrochloride solution neutralized beforehand to the pH of the buffer being used) was then added, followed by 10 ml of the 0.2% chloroform solution of disulfide. After vigorous shaking for 3-4 min, the brown chloroform extract of copper 8-mercaptoquinolinate was separated, filtered through a plug of cotton wool, and its optical density measured in a FÉK-M photocolorimeter, using a 1 cm cuvette and a blue filter. The percentage copper extracted was calculated by means of a calibration curve constructed beforehand, in almost neutral solutions of copper using excess 8-mercaptoquinoline. As is evident from Fig. 1 (Curve 2), when ascorbic acid is used, copper is completely extracted over the pH range 2.19 to 13, while in the presence of hydroxylamine it is completely extracted over the range 4 to 11.5 (Curve 3), and in the presence of the theoretical amount of thiooxine over the range 2 to 14 (Curve 1). Ascorbic acid permits the determination of copper in more acid solutions; this is very important, particularly during the determination of copper in salts which readily hydrolyze. It was observed, however, that ascorbic acid also slowly reduces the disulfide to 8-mercaptoquinoline. In the presence of very high concentrations of certain metals (particularly Fe, Ni, and Co), during prolonged extraction, these metals pass into the extract. This occurs to a considerably smaller extent when hydroxylamine is used as the reducing agent.

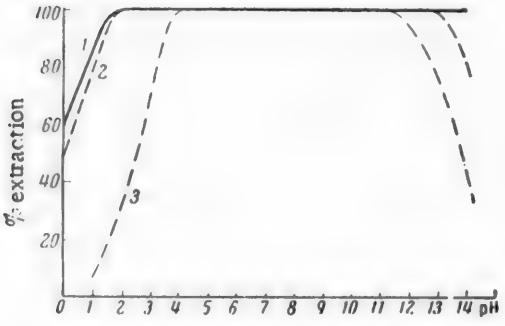


Fig. 1. The relation between the extractability of copper 8-mercaptoquinolinate and the pH of the medium and the nature of the reducing agent. 1) The theoretical amount of 8-mercaptoquinoline; 2) disulfide in the presence of ascorbic acid; 3) disulfide in the presence of hydroxylamine. a) % extraction.

The Sensitivity of the Method and Conformity of the Chloroform Extracts to Beer's Law. In order to study the conformity of the chloroform extracts of copper 8-mercaptoquinolinate to Beer's law, the reaction was carried out in solutions buffered with sodium acetate (pH 5-6). In view of the wide pH range over which copper 8-mercaptoquinolinate is extracted (pH 2-12) strict observation of the pH value is not important. The optical density of the extract, after filtration through cotton wool, was measured in a 1 cm cuvette on a SF-4 spectrophotometer at 432 mμ, or in a FÉK-N-54 photocolorimeter with a violet filter. The reference solution was an extract obtained in the same way but in the absence of copper. All the reagents used were carefully purified from copper as described below. As is evident from Fig. 2, chloroform solutions of copper 8-mercaptoquinolinate conform to Beer's law up to 8 μg Cu in 1 ml of chloroform when the measurements are made on a FÉK-N-54 photocolorimeter. At higher copper concentrations, the calibration curve deviates slightly from linearity. In practice, copper can be determined in concentrations up to 13 μg of Cu in 1 ml of chloroform.

TABLE 1

Determination of Copper in Pure Solutions

Cu taken, μg	Cu found, μg				Mean error, %
5	5,1	4,8	4,9	5	—1
20	19	20,5	21	21,5	+2,5
50	49	51	50	50	0
100	98	100	99	97	—1,5

The molar extinction coefficient of chloroform solutions of the copper complex at 432 mμ is 9500 [1].

Determination of Copper in Pure Solutions. In view of the wide pH range within which copper 8-mercaptoquinolinate can be extracted, copper can be determined in both acid and alkaline solutions. The possibility of varying the reaction conditions over a wide range is a very important advantage of this method of determining copper. It means, for example, that copper can be determined in ammoniacal solutions in the presence of appreciable amounts of the platinum metals; such a determination cannot be carried out in acid solutions. After acid decomposition the test solution is usually acid.

The greater part of the acid can be conveniently neutralized with sodium acetate. Alkaline and ammoniacal solutions are only to be recommended in the presence of predominating amounts of the platinum metals and other metals which exist in alkaline media in a stable anionic form.

The experiments described blow for the determination of copper in pure solutions were carried out in a weakly acid medium at pH 5-6. The experimental procedure was the same as that used for construction of a calibration curve. As the results in Table 2 show, varying amounts of copper can be determined with an error from -1.5 to +2.5%. Such an accuracy is quite adequate for the determination of small amounts of copper.

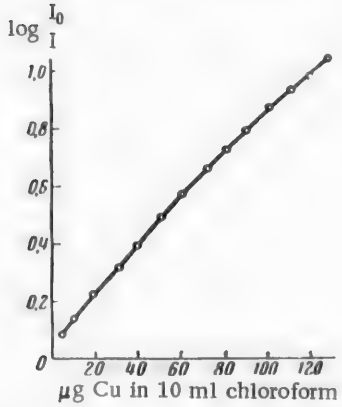


Fig. 2. Conformity of chloroform extracts of copper 8-mercaptoquinolinate to Beer's law (FEK-N-54 photocolorimeter, violet filter).

Determination of Copper in the Presence of Other Elements. Reagents: 1) 0.2% solution of disulfide in chloroform*. The solution is stored in the dark. It is desirable that the disulfide solution should not be kept for more than two weeks, and should be stored in a bottle covered with black paper; 2) 50% hydroxylamine hydrochloride solution; 3) 20% ascorbic acid solution; 4) 50% sodium acetate solution; 5) 20% sodium tartrate solution, ammonia, NaOH solution, and acid.

Purification of Reagents. All reagents used should be carefully purified from copper, and this can be done as follows. To 200-300 ml of sodium acetate or tartrate contained in a separating funnel is added 5 ml of hydroxylamine hydrochloride solution, and any copper is extracted with 2-3 portions of 30-40 ml of the chloroform solution of disulfide until the extract is colorless. Hydroxylamine hydrochloride and ascorbic acid solutions which have been neutralized to pH 4 are purified (when necessary) in a similar way. Hydroxylamine and ascorbic acid solutions with a pH 4 are unstable and should be prepared daily. It is best therefore to use high purity preparations (free from copper) so that there is no need for purification. Ammonia and the acids required are distilled. NaOH solutions can be freed from copper in this way as long as their concentrations are not higher than 0.5 N.

20-30 ml of test solution (hydrochloric, nitric, sulfuric acid solutions, etc, see Note 1) is placed in a 150 ml separating funnel and is neutralized with alkali to pH 1-2; sodium acetate is then added until the pH is 5-6

* The 8,8'-diquinolydisulfide should dissolve in chloroform to give a colorless solution. When a yellow or brownish colored solution is obtained, it is purified as follows. Ten g of 8,8'-diquinolyldisulfide is dissolved in 20 ml of concentrated hydrochloric acid and 5 g of sodium hypophosphite added. The solution is boiled for 5 min, cooled, diluted with water to 200 ml, and neutralized with sodium carbonate solution to a pH of 5. A bright-red crystalline precipitate of thiooxine dihydrate $C_9H_7NS \cdot 2H_2O$ separates out; the latter is purified from heavy metals as described in the paper by I. A. Shevchuk and E. A. Luksha [Izvest. Akad. Nauk Latv. SSR, No. 2, 127 (1961)]. The purified thiooxine dihydrate is converted into the disulfide by the method described in the paper cited.

TABLE 2

Determination of Copper in the Presence of Other Elements (20 μg copper was present in a final volume of 50 ml)

Foreign element (me), mg	Ratio Cu/me	Cu found, μg	Error, %	Foreign element (me), mg	Ratio Cu/me	Cu, found, μg	Error, %
Fe^{2+} 1100	1 : 55 000	20,8	+4	In^{3+} 280*	1 : 14 000	20	0
Ni^{2+} 4000	1 : 200 000	20,2	+1	Th^{4+} 500*	1 : 25 000	20	0
Co^{2+} 1500	1 : 75 000	20	0	La^{3+} 300*	1 : 15 000	20,2	+1
Cd^{2+} 2000	1 : 100 000	19,5	−2,5	Zr^{IV} 1000	1 : 50 000	19,8	−1
Mn^{2+} 2000	1 : 100 000	20,1	+0,5	Os^{VIII} 7,5	1 : 375	19,6	−2
Mo^{VI} 5000	1 : 250 000	20	0	Ru^{III} 5	1 : 250	19,7	−1,5
Bi^{3+} 2000	1 : 100 000	19,4	−3	Pt^{IV} 15**	1 : 750	20	0
Sb^{3+} 3000	1 : 150 000	19,6	−2	Pt^{IV} 3	1 : 150	19,9	−0,5
W^{VI} 5000	1 : 250 000	20,3	+1,5	Ta^{V} 40*	1 : 2 000	20,7	+3,5
Cr^{3+} 1300	1 : 65 000	20,1	+0,5	Nb^{V} 7,5*	1 : 375	20,1	+0,5
Pb^{2+} 6000	1 : 300 000	20	0	Ti^{IV} 800	1 : 40 000	19,5	−2,5
Tl^{+} 1000	1 : 50 000	20	0	Ge^{IV} 1000	1 : 50 000	20	0
Sn^{IV} 5000	1 : 250 000	19,8	−1	Te^{IV} 3	1 : 150	20,2	+1
As^{III} 600	1 : 30 000	20,2	+1	Hg^{2+} 250***	1 : 12 500	19,8	−1
As^{V} 2000	1 : 100 000	20	0	Se^{IV} 0,5	1 : 25	20,1	+0,5
V^{V} 300	1 : 15 000	20,2	+1	Pd^{2+} 50**	1 : 2 500	20,7	+3,5
Zn^{2+} 4000	1 : 10 000	19,5	−2,5	U^{VI} 2000	1 : 100 000	20,2	+1
Al^{3+} 1000	1 : 50 000	20,1	+0,5	Ag^{+} 560***	1 : 28 000	19	−5
Mg^{2+} 2000	1 : 100 000	19,5	−2,5	Rh^{III} 60*	1 : 3 000	19	–
Ga^{3+} 500*	1 : 25 000	20	0				
Re^{VII} 10*	1 : 500	20,3	+1,5				

* The limiting permissible amount was not established.

** In an ammoniacal medium at pH 8-9 in the presence of NH_4Cl.

*** In the presence of KI.

(see Note 2). Five ml of hydroxylamine or ascorbic acid solution is added (see Note 3), and the copper is extracted with 5 or 10 ml of the chloroform solution of disulfide, by vigorous shaking for 3-4 min. The yellow-brown extract is filtered through a plug of cotton wool, and the optical density measured in a 1 cm cuvette on a spectrophotometer at 432 mμ, or on a photocolorimeter with a blue or violet filter. The amount of copper is determined by means of a calibration curve which has been constructed using pure solutions of copper and all the reagents mentioned above.

Notes: 1. As will be shown below, high concentrations of chlorides, sulfates, nitrates, and other anions do not affect the accuracy of copper determination. Consequently, aliquots of test material (minerals, ores, steels, alloys, etc) can be dissolved in any acid. Any oxidizing agents present in solution are removed by excess hydroxylamine or ascorbic acid solutions.

2. During the determination of traces of copper in iron, aluminum, antimony, bismuth, titanium, zirconium, chromium, germanium, etc. and their salts, sodium tartrate can be used for preventing their hydrolysis in solution at pH 5-7. It is best to add the 20% sodium tartrate solution to the acid test solution first, and only then adjust the pH to 5-6. When this procedure is adopted Sb, Bi, and Ti hydroxides, which are difficult to dissolve, are not precipitated. When germanium is present, tartrate is added to the alkaline solution of germanic acid, and the pH then adjusted to 5-6. When the tartrate concentration of the solution is very high (particularly in alkaline media) some of the copper is also complexed, but in a weakly acid medium (ph 4-5), 3-4 ml of the 20% sodium tartrate solution in a total volume of the test solution of 50 ml does not affect the extraction of the copper. At pH 6-7, when the amount of tartrate mentioned above is present, copper extraction is slowed down somewhat; accordingly, in order to extract the copper completely, the time for which the extraction is carried out must be increased to 5 min.

TABLE 3

The Effect of Anions on the Accuracy of Copper Determination (20 μg of Cu was present in a volume of 50 ml; pH 5)

Anions, mg	Cu found, μg	Error, %
Oxalate 4	20.5	+2.5
Oxalate 1000(pH 8)	19.5	-2.5
Citrate 1320	20.3	+1.5
Tartrate 2500	20	0
Fluoride 80	21	+5
Iodide 7000	19.6	-2
Phosphate 3750	19.4	-3
Borate (saturated solution of $Na_2B_4O_7 \cdot 10 H_2O$	20.2	+1
Sulfate (saturated solution of Na_2SO_4)	20	0
Nitrate (saturated solution of $NaNO_3$)	20.5	+2.5
Perchlorate (saturated solution of $NaClO_4$)	19	-5
Bromide (saturated solution of NaBr)	19.7	-1.5
Thiosulfate	19	-5
Chlorate 0.39 (pH 5)	19.2	-4
Chlorate 5000 (pH 8)	20.3	+1.5
Thiocyanate 500	18.5	-7.5
Thiocyanate 100	19.2	-4
Cyanide 500	0	-100

When very large amounts of iron are present, 5 ml of the 20% tartrate solution is used, since when such amounts are present iron tartrate is precipitated and this interferes with extraction of the copper and removal of the extract. Large amounts of iron (1100 mg) slow down extraction of copper to some extent, so that the duration of the extraction should be increased to 5 min. Citrates readily keep Sb, Bi, Ti, and Fe in solution, but hinder extraction of copper to some extent, and they cannot therefore be recommended for this purpose.

In order to determine traces of copper in metallic antimony, bismuth, or their salts, 10 g of the salt is dissolved on heating in 50 ml of a 15% sodium tartrate solution having a pH of 5-6. A clear solution is obtained, from which copper is quantitatively extracted as indicated. In the given instance, this amount of tartrate does not interfere with extraction of copper in the presence of the amounts of antimony or bismuth indicated, since the main bulk of the tartrate is combined with these metals.

3. Apart from the amount of ascorbic acid or hydroxylamine solution taken for reducing copper to its univalent state, enough of these reducing agents should be taken to reduce all those components present in the solution (Fe^{3+}, CrO_4^{2-}, etc) which can be reduced by them. When small amounts of copper (2-3 μg) are present, it is best to use ascorbic acid, since hydroxylamine does not completely reduce copper in very dilute solutions (2-3 μg in 50 ml). As a consequence of this, the results may be 20% too low.

Limitation of the Method. Platinum Metals, Gold, Silver, and Selenium. Some of these elements (Pd, Ag, Au) are reduced to the elemental state by hydroxylamine in weakly acid solutions, or to lower valence states (Os, Ru). The sparingly soluble precipitates which are thereby formed entrain some of the copper. This is true for Pd, Pt, Au, Ag, and Se. Ho, Os, Ru, Rh, and Ir are not precipitated in weakly acid (pH 5-6) and neutral solutions, and do not interfere with determination of copper when they are present in moderate amounts. In general, formation of a solid phase in the test solution is not desirable, since under such conditions, part of the copper is lost. It is different in an ammoniacal medium, whereby platinum, palladium, and selenium are not reduced at a pH of 8-9 in the presence of several grams of NH_4Cl. Under such conditions, it is possible to mask 50 mg Pd, 15 mg Pt, and 0.5 mg selenium.

Gold and silver, even when present in very small amounts, are reduced by ascorbic acid to the elemental state, and entrain appreciable amounts of copper. Gold and silver can be complexed into very stable complexes by means of thiosulfate in an ammoniacal medium, and the gold and the silver in these complexes are not reduced by hydroxylamine and ascorbic acid. Thiosulfate ions, however, also complex copper so that very low results are obtained for the latter. Potassium iodide is a strong masking agent for silver and mercury. 20-30 ml of 50% KI solution can mask 560 mg silver and 250 mg mercury. In the presence of this amount of mercury extraction should not be carried out for more than 4 min.

Effect of High Concentrations of Other Elements. As mentioned above, when a spectrophotometer is used, the minimum amount of copper which can be reliably determined (with an error of 5-7%) is 2 μg. The reaction is slightly less sensitive than other methods, e. g., the dithizone or diphenylcarbazone methods. In this connection, during the determination of very small amounts of copper in pure metals, of particular importance is the

TABLE 4

Determination of Copper in Synthetic Mixtures (20 and 100 μg Cu taken in a total volume of 50 ml of test solution)

Foreign element, mg	Cu found, mg	Error, %
Sb—50, Bi—50, Mo—50, Ti—3, Zr—20, Fe—20, Pb—50, Zn—30	20,1	+0,5
	98,1	—1,3
Co—10, Mn—50, Zn—50, V—20, Cd—20, Fe—50, Zr—50, Cr—20	20,2	+1
	100	0

fact that it is possible to take large aliquots of test metal. When certain foreign metals are present in large amounts in the solution, difficulties may arise either as a result of hydrolysis, or sometimes as a result of transfer of the metal (Fe, Co, Ni) into the extract following upon substitution of the copper in the 8-mercaptoquinolinate.

Magnesium does not react with 8-mercaptoquinoline, but at high magnesium salt concentration, at pH 5-6, as a result of partial hydrolysis, basic salts are formed which interfere with separation of the extract. Ammonium chloride can usually be used for preventing hydrolysis in this case. Five g of NH_4Cl should be used for a solution containing 2 g Mg.

Aluminum. Determination of traces of copper in large aliquots of aluminum must be carried out at pH 4, since at pH 5-6 the aluminum salts hydrolyze to an appreciable extent. Sodium tartrate can be used for preventing precipitation of the basic salts, but when large amounts of the former are used, as mentioned already, extraction of copper is slowed down to some extent.

Nickel and Cobalt, too, in relatively moderate amounts (e. g. 50 mg), in the presence of large amounts of iron, color the solution rose when extraction is carried on for a long time (5-6 min). Nevertheless, traces of copper can be determined in the presence of large amounts of nickel and cobalt against a background of iron, as long as the extraction is only carried out for not more than three minutes, and the extract is removed immediately.

TABLE 5

Coprecipitation of Copper Thiooxinate with 8,8'-Diquinolyldisulfide

Disulfide, mg	Cu taken, μg	Cu found, μg	Disulfide mg	Cu taken, μg	Cu found, μg
50	12,7	13,2	10	12,7	12,7
50	—	~ 1	10	—	~ 1
25	12,7	12,8	5	12,7	12,0
25	—	~ 1	5	—	~ 1

TABLE 6

Coprecipitation of Copper from Solutions of Cobalt and Manganese Salts by Means of 8,8'-Diquinolyldisulfide

Metal, g in 300 ml	Cu taken, μg	Cu found, μg
Co^{2+} — 15	5	4,5
Co^{2+} 15	5	4,9
Co^{2+} 15	5	4,8
Mn^{2+} — 30	5	5,1
Mn^{2+} 30	5	4,4
Mn^{2+} 30	5	4,5

Tin and Titanium in their lower valence states (Sn^{II} and Ti^{III}) should be absent, since they vigorously reduce the disulfide to 8-mercaptoquinoline. Under these conditions tin forms a 8-mercaptoquinolinate which is extracted to give a yellow colored solution. Titanium does not form a compound with the reagent, but the 8-mercaptoquinoline formed reacts with many metals, as a result of which the reaction for copper loses its selectivity. In view of this, tin and titanium should be oxidized to the quadrivalent state by bromine, excess of which is removed by means of ascorbic acid or hydroxylamine. Sodium tartrate is used to prevent hydrolysis at pH 5-6.

The other elements in the amounts indicated in Table 2 do not lead to difficulties during the determination of copper.

Effect of Anions. Cyanides and thiocyanates should be absent; small amounts of oxalates (at pH 8 and higher, oxalates do not interfere), thiosulfates and chlorates (the latter in acid solution) can be tolerated. In alkaline media, chlorate ions like other oxidizing anions, do not interfere even in saturated solutions.

Table 3 contains the results for the determination of copper in the presence of various anions.

Determination of Copper in Synthetic Mixtures. Copper has been determined in various synthetic mixtures by means of the analytical procedure described above. Sodium tartrate was used for preventing the precipitation of several elements (the precipitation follows upon the hydrolysis of their salts). Table 4 contains some results for the determination of copper in synthetic mixtures.

The Use of 8,8'-Diquinolyldisulfide as a Selective Coprecipitant*. In order to determine very small amounts of copper in large volumes of solutions, when large aliquots of metals or their salts are taken, the copper must be concentrated beforehand. The disulfide, which is insoluble in weakly acid or alkaline aqueous solutions, and coprecipitates copper 8-mercaptoquinolinate, is a very selective coprecipitant for copper. The reagents used in the experiments described below were carefully purified from traces of copper. Copper was separated by coprecipitation as follows. To 500 ml of water containing a known amount of copper was added 10 ml of a 10% aqueous solution of ascorbic acid, 20 ml of a 20% solution of sodium acetate, and finally a solution of disulfide in pyridine with a concentration of 25 mg/ml. The disulfide precipitate plus the coprecipitated copper 8-mercaptoquinolinate were filtered off on a Gooch crucible fitted with filter paper. The crucible plus filter and precipitate were dried at 120° and the precipitate plus filter then transferred to a test tube, in which the precipitate (disulfide plus copper 8-mercaptoquinolinate) was dissolved in 5 ml of chloroform. The solution was filtered through a plug of cotton wool into a 1 cm cuvette, in which its optical density was measured on a SF-4 spectrophotometer at 432 mμ. The amount of copper was determined by means of a calibration curve constructed beforehand. As is evident from Table 5, the results obtained were satisfactory. For complete coprecipitation of copper, one hour should elapse from the moment at which disulfide is added to the test solution.

Coprecipitation of gamma amounts of copper in the presence of foreign metals was carried out in the same way, but instead of a pyridine solution of disulfide, a dioxane solution of disulfide (6 mg/ml) was used, since at the moment when pyridine is added some of the foreign metals are precipitated as their hydroxides. The salt of the foreign metal was subjected to careful purification from copper by the same method. When high concentrations of heavy metals are present, part of the metals is precipitated as their 8-mercaptoquinolinates. Accordingly, the precipitate was dissolved in a mixture of concentrated hydrochloric acid and hydrogen peroxide. The copper content of the solution obtained was then determined colorimetrically by the method described above. The precipitate plus the filter was transferred to a beaker and dissolved on heating in a mixture of 1 ml of concentrated hydrochloric acid and four drops of concentrated H_2O_2. The completely clear liquid obtained was heated until all the H_2O_2 had decomposed, and was then transferred into a separating funnel. One ml of 20% ascorbic acid solution was added, followed by 25% sodium acetate solution until the pH was about 5. The total volume of the aqueous phase in the separating funnel was 7-8 ml. The copper was extracted with 5 ml of a 0.2% chloroform solution of disulfide. The extract was filtered through a plug of cotton wool, and its optical density measured in a 1 cm cuvette on a SF-4 spectrophotometer at 432 mμ. The amount of copper was determined by means of a calibration curve. As is evident from Table 6, the experimental results can be regarded as satisfactory.

When 1 ml of the extractant solution is used (0.2% chloroform solution of disulfide) for extracting copper, it is possible to determine from 0.1 to 1 μg of copper by this method.

Hydroxylamine can be used instead of ascrobic acid as a reducing agent.

SUMMARY

A description is given of a photometric method for the determination of copper, which is based on the interaction of cuprous ions (in the presence of an excess of a reducing agent—hydroxylamine or ascrobic acid) with 8,8'-diquinolyldisulfide to form cuprous 8-mercaptoquinolinate $CuC_9H_6NS \cdot C_9H_6NSH$.

The reagent is a highly selective one for copper. Even in the absence of excess reagent, the reaction is quantitative over a very wide pH range of 2.19 to 13 in the presence of ascrobic acid, and from 4 to 11.5 in the presence of hydroxylamine; this is possible because of the high stability of the copper complex.

The sensitivity of the reagent does not change in the presence of several masking agents, e. g., tartrates, which can therefore be used for keeping in solution those salts which tend to hydrolyze readily in weakly acid and alkaline solutions.

The reaction is quantitative even in ammoniacal solutions (not more than 5% NH_4OH) so that ammonia can be used in some instances keeping certain elements in solution in alkaline media.

Very large amounts of Fe, Ni, Co, Cd, Mn, Mo, Bi, Sb, W, Cr, Pb, Tl, Sn^{IV}, As, V, Zn, Al, Mg, Ga, Re, Zr, In, Th, La, Ti, the alkali and alkaline earths do not interfere with the determination of gamma amounts of copper. Pt, Ru, and Os ions can be tolerated in amounts which are 150-400 times that of copper, and Se ions in

* The experimental work was carried out by L. M. Rengart.

amounts which are 25 times that of copper. Gold should be absent since it is reduced by ascorbic acid to the elemental state, and coprecipitates part of the copper.

High concentrations of most of the common anions (chlorides, bromides, iodides, fluorides, sulfates, phosphates, nitrates, chlorates, perchlorates, borates, and tartrates) do not affect the accuracy of copper determination. Thiocyanate interferes with extraction of copper to some extent; cyanide ions should be absent.

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DETERMINATION OF THE INSTABILITY CONSTANT OF THE COMPLEX OF BERYLLIUM WITH ETHYLENE-DIAMINETETRACETIC ACID

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There is no information in current textbooks [1] or in the periodical literature on the instability constant of the compound of beryllium with ethylenediaminetetracetic acid (EDTA-H_4Y). Pribil [2] has indicated that this complex is a very stable one, while some research workers have assumed that such a compound does not exist. The disodium salt of EDTA (EDTA-Na)—so called Complexon III—has already found wide application for the determination of beryllium, and is specified in a number of analytical procedures [3]. The absence of any information on $K_{inst.}$ of the compound of beryllium with EDTA renders these procedures empirical, and means that new procedures cannot be developed.

Attempts to use spectrophotometric methods both for determining beryllium by means of EDTA-Na [4], and for studying the interaction between beryllium and this reagent, were unsuccessful [5]. Our preliminary experiments showed that the maximum light absorption of both EDTA-Na and of its complex with beryllium lies in the far ultraviolet, which is not covered by apparatus such as the SF-4, while the descending sections of the curves, which are covered by the SF-4, do not differ enough from each other.

TABLE 1

Experimental Results Used for Calculating the Characteristics of the Exchange of H^+ ions for Be^{2+} ions. $\mu = 0.05$, $f_1 = 0.85$

g, c	V, ml	Initial conditions		Equilibrium conditions		
		pH°	$c^{\circ}_{Be} \cdot 10^3$/ml	pH	$c_1 \cdot 10^3$ M	$c_2 \cdot 10^3$ M
0,2	100	2,18	10	2,05	1,05	7,82
0,2	50	2,05	9	1,80	1,86	5,44
0,5	100	2,18	10	1,90	1,48	4,67
0,5	100	2,18	10	1,90	1,48	5,00
0,8	100	2,23	10	1,70	2,34	2,99
1,0	100	2,23	10	1,76	2,33	2,70
1,5	100	2,23	10	1,60	2,95	0,99

It was decided therefore to use an ion exchange method, the theory of which has been developed in sufficient detail [6]. We considered that it would be impossible to determine the composition of the compound formed, and assumed that it is 1 : 1, since we could not find a published reference to any other composition for divalent metals and comparatively dilute solutions.

We decided to work with fairly acid solutions (pH $\cong$ 2), in order to eliminate complications arising from hydrolysis of the Be^{2+} ion. Under these conditions, according to Schwarzenbach [7], the complex compounds formed are of the type $MeHY^-$. The problem therefore only consisted in determining the instability constant of the complex $BeHY^-$.

Reagents, Apparatus, Experimental Technique. The cation exchange resin KU-1, the H-form, was used; the particle size of this resin was 0.25-0.5 mm, it was washed and dried at 70° prior to use. Beryllium solutions were prepared from $BeSO_4 \cdot 4H_2O$ chemically pure grade, which had been recrystallized twice from water. The concentration of the stock solution was checked gravimetrically (precipitated as $Be(OH)_2$ and weighed as BeO).

The working solutions were prepared by dilution of the stock solution; their concentrations were established photometrically [8] on a FÉK-M apparatus; when the system contained EDTA-Na, its effect was eliminated, so that a determination in this case gave the sum of simple Be^{2+} ions and those ions complexed by ethylenediaminetetracetic acid. The EDTA-Na solution was prepared by dissolving an accurately weighed aliquot of the twice recrystallized commercial product $Na_2H_2Y \cdot H_2O$.

The initial value of the ionic strength of all the solutions was constant and equal to about 0.05, while the final value was about 0.04. The ionic strength was maintained constant by suitable selection of the initial concentrations of all the components of the system, not by adding an indifferent electrolyte. The values of the activity coefficients required for the calculations were taken from the textbook by Lur'e [9].

The pH values were measured with a glass electrode (with a tube amplifier) which had been calibrated against the hydrogen electrode.

The experimental temperature was 25 ± 1°.

Ion exchange was carried out under static conditions by mechanical agitation of an aliquot of the cation exchange resin with a known volume of the test solution for four hours—this time proved sufficient for equilibrium to be established. The amount of cation exchange resin taken did not exceed 1.5 g, while the volume of the solution was 100 ml in most cases; correction for swelling of the resin was negligible and was ignored.

Experimental Results. First of all it is necessary to determine the exchange constant of H^+ ions for Be^{2+} ions, ($K_{exchange}$), and the maximum capacity (α_m) of the KU-1 cation exchange resin for Be^{2+} ions. The ion exchange process can be represented thus:

$$HR + {}^1/_2Be^{2+} \rightleftarrows {}^1/_2BeR_2 + H^+.$$

Denoting the equilibrium content of H^+ and Be^{2+} ions in the adsorbent by α_1 and α_2 mg · equiv./100 g respectively, and the equilibrium concentration of the same ions in solution by c_1 and c_2 M respectively, and finally letting $K^{-1}_{exchange} = K'_{exchange}$, we get

$$a_1 = K'_{ex}\left(\frac{a_2}{c_2}\right)^{1/2} \cdot c_1. \qquad (1)$$

Bearing in mind that the values c_1 and c_2 are experimental values, $\alpha_1 = \alpha_m - \alpha_2$, and in turn $\alpha_2 = (c^0_{Be} - c_2) \cdot V \cdot 200/g$, where c^0_{Be} is the initial beryllium concentration in solution (m), V is its volume (in ml), while g is the amount of cation exchange resin taken (in g), then rewriting (1);

$$a_2 = a_m - K'_{ex}\left(\frac{a_2}{c_2}\right)^{1/2} \cdot c_1, \qquad (2)$$

it is evident that the unknown parameters in the equation for the straight line (2)— α_m and $K'_{exchange}$ —can be found either graphically or by the method of mean squares, from the experimental results.

The experimental results are given in Table 1. The most probable values of the exchange constant of H^+ ions for Be^{2+} ions and the maximum capacity of the KU-1 resin for Be^{2+} ions were found to be $K'_{exchange} = 11.5$ and $\alpha_m = 236$ mg · equiv./100 g respectively; these values were calculated from the experimental results by the method of least squares.

One can next proceed to determine the instability constant of beryllium ethlenediaminetetracetate, which, being an anion, is not absorbed by the cation exchange resin. A series of mixtures with a constant ionic strength, and known values of pH^0, c^0_{Be}, and $c^0_{Na_2HY}$ were shaken with a known amount of cation exchange resin. After equilibrium had been established, the new values of the pH and of c'_{Be} = total of complexed and uncomplex beryllium particles were determined, i. e.

$$c'_{Be} = [Be^{2+}]' + [\text{complexed}],$$

where $[Be^{2+}]'$ denotes the sum of all the beryllium particles which have not been complexed. From (1) we obtain:

$$c_2 = [Be^{2+}]' = (K'_0)^2 \cdot \left(\frac{c_1}{a_2}\right)^2 \cdot a_2. \qquad (3)$$

TABLE 2

Results Used for Calculating $K_{instab.}$ for Beryllium Ethylenediaminetetracetate; $\mu \cong 0.05$; $f_1 = 0.85$; V=100 ml; g = $= 0.5_g$; $K'_{exchange} = 11.5$; $\alpha_m = 236$

$c^0_{Be} \cdot 10^3$ M	$c^0_{Na_2H_2Y} \cdot 10^3$ M	pH°	$c'_{Be} \cdot 10^3$ M	pH	$K_{instab.} 10$
8,0	2,3	2,45	3,40	1,95	1,10
8,0	2,3	2,45	3,38	1,95	1,71
7,5	3,0	2,33	3,24	1,93	1,04
7,5	3,0	2,33	3,22	1,93	1,18
7,0	3,7	2,28	3,08	1,88	1,12
7,0	3,7	2,28	2,90	1,87	2,16
6,0	5,0	2,35	2,36	1,97	2,14
6,0	5,0	2,35	2,40	2,05	1,91

$K_{instab.} = (1,5 \pm 0,2) \cdot 10^{-9}$

This expression permits $[Be^{2+}]'$ to be calculated, since $K'_{exchange}$ is known, and $c_1 = [H^+]$ is found directly by experiment,

$$a_2 = \frac{(c^0_{Be} - c'_{Be})\, V \cdot 200}{g} \text{ and } a_1 = a_m - a_2.$$

The instability constant of the complex $BeHY^-$ was calculated by the formula:

$$K_{inst.} = \frac{[Be^{2+}]' \cdot \beta\, [HY^{3-}]' \cdot \alpha}{[BeHY^-]}, \qquad (4)$$

where $[HY^{3-}]'$ is the sum of all the particles of EDTA-Na not bound as a complex; $[HY^{3-}]' = c^0_{Na_2H_2Y} - (c'_{Be} - c_2)$. The equilibrium concentration of the complex $[BeHY^-] = c'_{Be} - c^2$. The coefficient β is the fraction of Be^{2+} ions in the total of the uncomplexed beryllium particles. Taking into account the process [10]

$$Be^{2+} + H_2O \rightleftarrows BeOH^+ + H^+, \quad K_r = 2{,}32 \cdot 10^{-4}$$

an expression for β as a function of $[H^+]$ can be found:

$$\beta = \frac{[H^+]}{[H^+] + K_r}.$$

The coefficient α is the fraction of HY^{3-} ions in the total of all the uncomplexed particles of EDTA-Na. For a given pH it is calculated by means of the equation:

$$\alpha = \frac{1}{1 + \frac{[H^+]}{\varkappa_3} + \frac{[H^+]^2}{\varkappa_2\varkappa_3} + \frac{[H^+]^3}{\varkappa_1\varkappa_2\varkappa_3}},$$

in which $\alpha_{1 \ldots 3}$ are the constants for the stepwise acid dissociation of H_4Y [2]. The low pH value of 2 at which the work was carried out enables one to ignore the last fourth stage of dissociation.

Table 2 contains the experimental results and the values of $K_{instab.}$ for beryllium ethylenediaminetetraacetate calculated by means of them.

By using the mean value of this constant for calculating the amount of $Be(OH)_2$ precipitated by ammonia in the presence of excess EDTA-Na taking into account the processes:

$$BeHY^- \rightleftarrows Be^{2+} + HY^{3-} \qquad 1{,}5\cdot10^{-9}$$

$$Be^{2+} + 2OH^- \rightleftarrows Be(OH)_2 \qquad 10^{20}\ [11]$$

$$NH_4OH \rightleftarrows NH_4^+ + OH^- \qquad 1{,}5\cdot10^{-5}$$

it is possible to show that precipitation of a 0.1 M solution of a beryllium salt by 1 M ammonia solution in the presence of excess EDTA-Na is 99.7% complete. This, in general, agrees with the observations of many authors who have used this method of precipitation for analytical purposes.

It is interesting to note that if it is assumed that the composition of the complex is represented by BeY^{2-} and the experimental results obtained above are used, the value obtained for $K_{instab.}$ is of the order of 10^{-17}, which cannot explain the fact of the precipitation of $Be(OH)_2$ by ammonia from a solution containing EDTA-Na. A complex with such a constant should be very stable and should not be broken down by ammonia. This fact appears to be a confirmation of the correctness of our assumption that the composition of the beryllium complex is represented by $BeHY^-$.

SUMMARY

On the assumption that the composition of the complex formed between beryllium and EDTA is represented by $BeHY^-$, it has been established by ion exchange on KU-1 cation exchange resin that the instability constant of this complex is $1.5 \pm 0.2 \times 10^{-9}$.

Calculations in which this value of the constant is used give results which are in agreement with experimental data.

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GRAVIMETRIC DETERMINATION OF ZIRCONIUM AFTER ITS PRECIPITATION WITH CYCLOHEXANOL-1-CARBOXYLIC ACID

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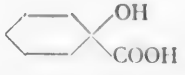
A large number of methods have been developed for the quantitative determination of zirconium using various organic precipitants; the latter include phenylarsonic acid [1], mandelic acid and its derivatives [2-7], phthalic acid [8], tetrachlorophthalic acid [9], fumaric acid [10], and also cupferron [11] and its analog N-benzoylphenylhydroxylamine [12]. In recent years new organic reagents containing the groups SeO_2H, TeO_2H, PO_3H_2 have been suggested for the determination of zirconium, and for its separation from other elements [13, 14]. Among these reagents, mandelic acid and its derivatives have proved to be very interesting since they possess high selectivity. In the work described here we have attempted to use an analog of this acid—cyclohexanol-1-carboxylic acid—as a precipitant for the determination of zirconium and for its separation from accompanying elements:



(cyclohexanol-1-carboxylic acid)

It was established that cyclohexanol-1-carboxylic acid, like mandelic acid, precipitates zirconium from a dilute hydrochloric acid solution while aluminum, iron, beryllium, thorium, uranium, vanadium, tin, titanium, chromium, and the rare earths do not interfere with the determination of zirconium.

EXPERIMENTAL

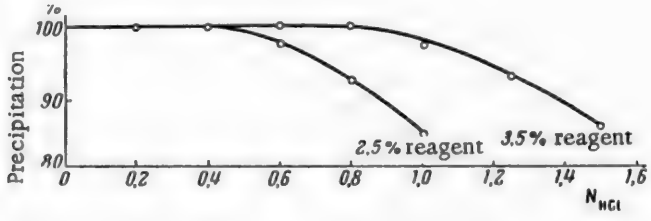
Synthesis of Cyclohexnol-1-carboxylic acid. Cyclohexnol-1-carboxylic acid was synthesized by a modified version of Ultee's method [15]. To 50 g of freshly distilled cyclohexanol was added an excess of a saturated solution of sodium bisulfite. The mixture was stirred until it had crystallized into a thick mass. The bisulfite compound was filtered off, washed with a small amount of water, and a saturated solution of potassium cyanide (25 g) added to the mixture obtained with vigorous stirring. After 20-30 min, when the reaction was complete, the nitrile of cyclohexanol-1-carboxylic acid separated out as an oil. The nitrile was removed to a separating funnel, in which it was heated with four times its amount of concentrated hydrochloric acid on a boiling water bath for 3-5 hours. The white crystalline material which separated out after cooling was the amide of cyclohexanol-1-carboxylic acid. The amide was next heated on a water bath with a small excess of a 10% sodium hydroxide solution for two hours until ammonia had ceased to be liberated. After cooling, the solution was acidified with hydrochloric acid and white crystalline cyclohexanol-1-carboxylic acid separated out. A fairly pure material can be obtained by recrystallizing the product from water. The melting point was 107° (in good agreement with published results). The solubility of the acid in water is 7.3 g/100 ml H_2O (20°). The compound is stable on standing in air; no decomposition was observed over a period of several months.

TABLE 1

Determination of Zirconium in Solutions of its Salts

Zr, g		Error		Zr, g		Error	
taken	found	g	%	taken	found	g	%
0,0024	0,0024	±0,0000	±0,0	0,0119	0,0118	−0,0001	−0,8
0,0024	0,0024	±0,0000	±0,0	0,0357	0,0358	+0,0001	+0,3
0,0119	0,0119	±0,0000	±0,0	0,0357	0,0356	−0,0001	−0,3

Optimum Conditions for Precipitating Zirconium. In order to establish the optimum precipitating conditions, a study was made of the effect of acid and reagent concentrations on the completeness of precipitation



Effect of HCl concentration and reagent concentration on completeness of zirconium precipitation.

of zirconium. For this purpose, various amounts of hydrochloric acid were added to a solution containing a known amount of zirconium, the solutions obtained were diluted with water to 25 ml, and 25 ml of a 5% solution (or 7% solution) of the reagent added; the final solution was heated to the boil. After the solution was cooled, the precipitate was filtered off and washed with 0.1 N hydrochloric acid containing 0.5% of the reagent. The precipitate was dried, calcined to constant weight at 1000°, and weighed as zirconium dioxide. The effect of acid and reagent concentrations on completeness of precipitation is shown in the diagram. The optimum conditions were found to be as follows: the hydrochloric acid concentration should not exceed 0.4 N when 2.5% reagent solution is used; or more than 0.8 N when 3.5% reagent solution is used. Precipitation can also be carried out in the presence of nitric or perchloric acid of the same normality. In the presence of sulfuric acid, however, as a result of the formation of stable $[ZrO(SO_4)_2]^{2-}$ ions, precipitation is incomplete. Tartrate and citrate ions, and other organic acids which give stable complex ions with zirconium, also interfere with complete precipitation of zirconium.

As the values given in Table 1 show, results for the determination of zirconium in solutions of its salts are reasonably accurate and exhibit good reproducibility.

The composition of the precipitates which separate out from solutions with different hydrochloric acid concentrations is variable. Zirconium ions are known to hydrolyze strongly and to polymerize even in acid solution. The ratio of metal to organic addendum in the precipitate separated from 0.5 N hydrochloric acid approximates to 1 : 1.7. The ratio of the metal to the addendum in the precipitate separated from 2 N hydrochloric acid approximates to 1 : 2, which corresponds to a formula of $ZrO(C_7H_{11}O_3)_2$ or $Zr(OH)_2(C_7H_{11}O_3)_2$.

Because the composition of the precipitate varies, the precipitate cannot be weighed after drying; it must be calcined to ZrO_2.

TABLE 2

Determination of Zirconium in the Presence of Foreign Ions

Zr, g		Foreign ions, g		Error	
taken	found			g	%
0,0119	0,0119	Al	0,012	±0,0000	±0,0
0,0119	0,0120		0,060	+0,0001	+0,8
0,0024	0,0024		0,024	±0,0000	±0,0
0,0119	0,0119	Be	0,027	±0,0000	±0,0
0,0119	0,0120		0,133	+0,0001	+0,8
0,0024	0,0025		0,133	+0,0001	+4,0
0,0119	0,0119	$Fe^{(III)}$	0,014	±0,0000	±0,0
0,0119	0,0120		0,143	+0,0001	+0,8
0,0024	0,0024		0,029	±0,0000	±0,0
0,0119	0,0120	Ti	0,017	+0,0001	+0,8
0,0119	0,0120		0,035	+0,0001	+0,8
0,0048	0,0048		0,035	±0,0000	±0,0
0,0119	0,0119	$Sn^{(IV)}$	0,018	±0,0000	±0,0
0,0119	0,0119		0,045	±0,0000	±0,0
0,0024	0,0025		0,045	+0,0001	+4,0
0,0119	0,0118	Th	0,011	−0,0001	−0,8
0,0119	0,0119		0,060	±0,0000	±0,0
0,0024	0,0023		0,060	−0,0001	−4,0
0,0119	0,0118	Total rare earths	0,011	−0,0001	−0,8
0,0119	0,0118		0,072	−0,0001	−0,8
0,0024	0,0024		0,072	±0,0000	±0,0
0,0119	0,0118	$U^{(VI)}$	0,012	−0,0001	−0,8
0,0119	0,0120		0,036	+0,0001	+0,8
0,0024	0,0025		0,050	+0,0001	+4,0

TABLE 3

Determination of Zirconium in Zirconium Bronze

Zr found, %	
mandelic acid method	suggested method
12,95; 13,10; 13,08	12,85; 13,05; 12,90

TABLE 4

Determination of Zirconium in Zircon

ZrO_2 found, %		
phenylarsonate method	mandelic acid method	suggested method
63.8	63.8	63.6
64.0	63.9	63.7

Determination of Zirconium in the Presence of Other Elements in an Alloy and in a Mineral. Zirconium can be readily separated from a number of elements such as aluminum, iron, beryllium, titanium, quadrivalent tin, thorium, sexivalent uranium, and the rare earths (Table 2). Hafnium is coprecipitated with zirconium.

The reagent is no less selective than mandelic acid. Considerably less of it is required for precipitating zirconium.

In order to determine zirconium in zirconium bronze, an aliquot of the latter is dissolved in nitric acid or in a mixture of the latter with hydrochloric acid. After the alloy has dissolved completely, the solution is carefully evaporated almost to dryness, a known amount of hydrochloric acid is then added and the solution diluted to 30 ml with water; 30 ml of a 5% solution of the reagent is added on heating; the precipitate is filtered off, washed, and then calcined to ZrO_2. The method gives satisfactory results.

For the analysis of zircon, 4 g of NaOH is fused in a nickel crucible until sputtering ceases. To the cooled melt a finely ground aliquot of zircon is added and the mixture fused at a dark-red heat until effervesence ceases. Heating is then stopped and 1 g of sodium peroxide added; fusion is continued until oxygen ceases to be evolved (approximately 30-40 min). Zirconium hydroxide is formed on treating the melt with water. The precipitate is filtered off and the filter plus precipitate placed in the beaker in which the melt was decomposed with water; 20 ml of concentrated hydrochloric acid is added, and the beaker heated on a hot plate until the hydroxide has dissolved; 20 ml of water is then added and the liquid filtered. The hydrochloric acid solution is transferred to a 100 ml standard flask, the filter is washed several times with water and the solution made up to the mark with water. The zirconium is determined by taking an aliquot of this solution and precipitating it by the method described above. Results for the determination of zirconium in zircon are given in Table 4.

SUMMARY

A new gravimetric method has been developed for the determination of zirconium, in which cyclohexanol-1-carboxylic acid is used as the precipitant. The precipitate formed has a variable composition. It is therefore calcined to ZrO_2.

It is possible, by means of this method, to determine zirconium in the presence of aluminum, ferric iron, beryllium, quadrivalent tin, titanium, thorium, sexivalent uranium, and the rare earths.

Satisfactory results were obtained when this method was used to determine zirconium in zirconium bronze and zircon.

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A STUDY OF THE COPRECIPITATION OF GERMANIUM WITH THE HYDROXIDES OF IRON AND OTHER METALS

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In recent years germanium has been separated by coprecipitation with ferric hydroxide [1-3]. We have carried out a more detailed study of this process using the radiochemically pure isotope of germanium Ge^{71}. In the course of this work the possibility of using coprecipitation of germanium in analytical practice was established in greater detail. At the same time the results obtained make it possible to come to some conclusions regarding the mechanism of the coprecipitation itself.

Radiometric measurments were made on a type B setup with a MST-17 torsion counter. The results were calculated on the basis of the difference between the radioactivities of the solutions before and after carrying out the operations, and also by comparing the activity of the solutions obtained with the activity of a reference solution. Absorption of radiation by the layer of the solution, and changes in volume were taken into account.

TABLE 1

Amount of Ge precipitated with $Fe(OH)_3$ from solution, %	Amount of Ge extracted from the $Fe(OH)_3$ precipitate by Na_2S solution, %
99	97
100	97
100	90
99	89

During a study of the progress of germanium coprecipitation as a function of the completeness of precipitation of ferric hydroxide, we had already shown that complete coprecipitation is tied up with the precipitation of all the iron. Germanium can be quantitatively extracted from solutions in which the germanium concentration is 2-10 μg/ml, when the ratio Fe : Ge is equal to or greater than 25. In contrast to opinions advanced earlier [1], it was established that the presence of a small excess of NH_4OH during the precipitation of ferric hydroxide is more likely to facilitate than hinder quantitative extraction of germanium.

It was also shown that complete extraction of germanium can be achieved by mixing ferric hydroxide precipitate, prepared beforehand, with the germanium solution; it was shown that extraction of germanium during this process differs somewhat from the case where germanium is coprecipitated with the ferric hydroxide as it is formed [4].

Stability with which Germanium is held by the Precipitate. The ferric hydroxide precipitate containing the coprecipitated germanium was treated with carbonic acid solution, ammonium carbonate, and hydrogen sulfide or sodium sulfide solutions. Carbonic acid and ammonium carbonate solutions hardly extracted any germanium; the hydrogen sulfide solution extracted the germanium very incompletely; germanium was readily and quantitatively extracted from the precipitate by sodium sulfide solution.

The experiments were carried out as follows. Germanium was coprecipitated from a solution containing 320 μg germanium with ferric hydroxide (25 mg Fe). The filtered hydroxide precipitate was washed three times

TABLE 2

Ge extracted with $Fe(OH)_3$ from solution, %	Ge extracted from the precipitate, %			Total germanium extracted from the precipitate, %
	wash liquor			
	I	II	III	
99	82	14	3	99
99	82	12	2	96
100	82	13	2	97
100	82	18	3	103

TABLE 3

(Amount of Ge 121 μg)

Salt present	Salt concentration, M	Amount		Ge extracted, %
		Iron, mg	NH_4OH, equivalents per equivalent of iron	
$NaNO_3$	3,8	5	5	100
NH_4NO_3	3,8	5	5	99
$Ca(NO_3)_2$	3,5	20	1,2	96
NaCl	3,8	5	5	99
NH_4Cl	3,5	20	1,2	97
$CaCl_2$	3,5	20	1,2	96

with water and then ten times with 5 ml 10% Na_2S solution. Since, as a result of partial peptization of the precipitate, some of the iron passes through the filter, the wash liquor was filtered a second time after standing for a period, and the filter washed once with 5 ml of fresh Na_2S solution. The results obtained are given in Table 1.

Taking into account the possibility of poor contact between the precipitate on the filter and the wash liquors, the experiments were repeated using another variant. The ferric hydroxide plus the coprecipitated germanium were separated by centrifuging rather than by filtration; the precipitate was then washed twice with water and three times with 5 ml of a hot 10% Na_2S solution, the precipitate being carefully mixed with the wash liquors each time. The wash liquors were collected separately and made up to 50 ml with water. The results obtained are given in Table 2.

These experiments confirmed that germanium is held sufficiently strongly by the ferric hydroxide. The fact that germanium can be washed out of the precipitate by means of Na_2S solution could find practical application for concentrating germanium and for purifying it from interfering impurities prior to its analytical determination.

Effect of Foreign Salts. A study was made of the extent to which germanium is coprecipitated with ferric hydroxide, in the presence of considerable concentrations of sodium, calcium, and ammonium nitrates, and sodium, ammonium, and calcium chlorides. The concentrations of the foreign salts varied within the limits 3,8-3,5 M. The results obtained are given in Table 3.

No significant decrease in the extent to which germanium is coprecipitated was observed in the presence of these salts. The small drop in completeness of coprecipitation in the presence of $Ca(NO_3)_2$, NH_4Cl and $CaCl_2$ can be explained on the grounds that at high concentrations of these salts, it is difficult to ensure quantitative precipitation of ferric hydroxide; a larger amount of iron was therefore taken for these experiments. It was also demonstrated that even high concentrations of NH_4OH (up to 15% calculated as NH_3) have no appreciable effect on the extent to which germanium is coprecipitated.

TABLE 4

Partial precipitation of Fe with NH_4OH		Partial dissolution of $Fe(OH)_3$ with H_2SO_4	
amount of NH_4OH expressed as equivalents per equivalent of Fe	Ge coprecipitated, %	amount of H_2SO_4 expressed as equivalents per equivalent of Fe	Ge coprecipitated, %
0,2	13	0,8	22
0,4	19	0,6	23
0,6	33	0,4	38
0,8	49	0,2	58
1,0	98		

TABLE 5

NH_4OH added, equivalents per equivalent of iron	Germanium extracted, %		
	with fresh precipitate	with precipitate which has stood for 2 hr on a water bath	with precipitate which has stood for 10 hr on a water bath
0,2	0	13	5
0,4	0	12	8
0,6	0	6	10
0,8	10	12	9
0,9	64	37	13
1,0	99	99	100

These experiments confirm that it is possible to extract germanium with ferric hydroxide in the presence of large amounts of foreign salts; this is very important from an analytical viewpoint. They also indirectly indicate that coprecipitation of germanium is not a simple adsorption process.

The next series of experiments were designed to explain the mechanism of the coprecipitation process.

Reversibility of the Coprecipitation Process. In one series of experiments, iron was precipitated from 50 ml of solution containing 125 μg germanium and 25 mg iron by various amounts of NH_4OH; the latter was added in amounts of 0.2, 0.4, 0.6, 0.8, and 1.0 equivalents with respect to iron. In another series the iron was precipitated by an exactly equivalent amount of NH_4OH, and H_2SO_4 solution was then added in amounts of 0.8, 0.6, 0.4, and 0.2 equivalents with respect to one equivalent of iron. The amount of coprecipitated germanium was determined in all the solutions after removal of the precipitate. The results obtained are given in Table 4 and in Fig. 1.

It is obvious that precipitation of germanium with ferric hydroxide is a fully reversible process. The small difference between the curves obtained during partial precipitation of iron (Curve 1), and partial dissolution of the hydroxide precipitate (Curve 2), does not exceed the experimental error, and is the result, presumably, of the fact that equilibrium is not completely established between the solution and the precipitate after addition of acid.

Effect of Precipitate Aging. The effect of aging of the hydroxide precipitate and the effect of basic iron salts on the coprecipitation curve was studied in three series of experiments. NH_4OH in amounts of 0.2, 0.4, 0.6, 0.8, and 1.0 equivalents with respect to iron were added to solutions containing 50 mg iron. The solutions were then allowed to stand in contact with the precipitates for 97 hours. In the first series the solution were kept for two hours out of the 97 on a boiling water bath, while in the second series they were kept for ten hours on a boiling water bath, and in the third series – the control series – the experiments were carried out with fresh precipitates.

After aging of the precipitates, the solutions were made up to 50 ml with water and added to 2 ml of solution containing 420 μg germanium. The precipitates were filtered after 15-20 min.

TABLE 6

NaOH added, equivalents per equivalent of metal	Germanium extracted, %		
	with $Mg(OH)_2$	with $Mn(OH)_2$	with $Cu(OH)_2$
0,2	98	98	7
0,4	99	98	15
0,6	100	97	95
0,8	98	99	89
0,9	99	99	—
1,0	99	98	85

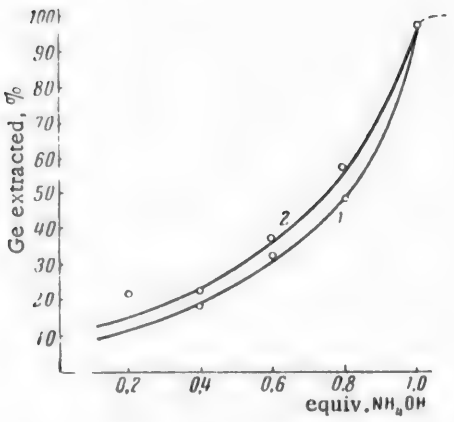

Fig. 1. Reversibility of coprecipitation of Ge. 1) Coprecipitation of Ge during partial precipitation; 2) coprecipitation of Ge during partial dissolution of the precipitate.

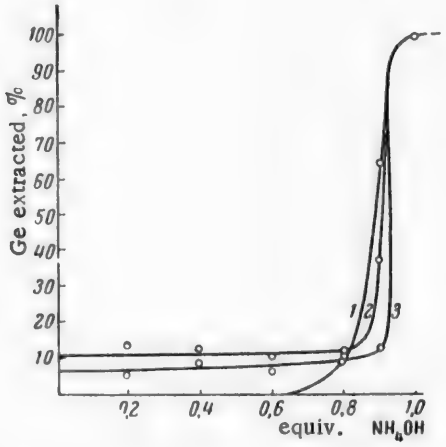

Fig. 2. Effect of precipitate aging on coprecipitation of Ge. 1) Fresh precipitate; 2) precipitate which has stood for 2 hr on a water bath; 3) precipitate which has stood for 10 hr on a water bath.

After filtration, the percentage germanium extracted from the solution was determined. The results obtained are given in Table 5 and in Fig. 2.

It is clear from these results that during the aging of the precipitates of the basic salts and hydroxide of iron, the germanium extraction curve approximates more and more to the vertical line near the equivalence point for the precipitation of ferric hydroxide. On the other hand, there is a characteristic "tail" to the germanium extraction curve during aging of the precipitates.

This phenomenon can be explained on the assumption that during aging of the precipitates, the composition of the latter becomes more homogeneous than that of freshly prepared precipitates, which contain basic salts of different compositions and with the hydroxide as an impurity. The pH jump also becomes sharper as a result of the buffering effect of the precipitates.

During aging, as a result of hydrolysis, almost all the iron is precipitated in the form of basic salts, even from solutions to which little NH_4OH has been added. The appearance of a "tail" is explained by simple adsorption of the germanium by the precipitate of basic iron salts which has a fairly significant volume. The precipitates of the basic salts which are obtained immediately after addition of 0.2, 0.4, and 0.6 equivalents of alkali have such a small volume, that adsorption of germanium could not be detected by the technique used.

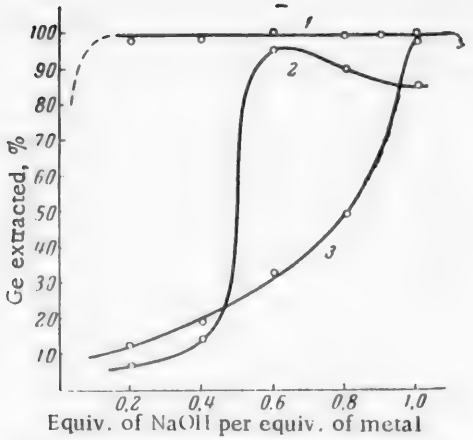

Fig. 3. Coprecipitation curves of Ge with various metals. 1) With $Mg(OH)_2$ and $Mn(OH)_2$; 2) with $Cu(OH)_2$; 3) with $Fe(OH)_3$.

Coprecipitation of Germanium with Magnesium, Manganese, and Copper Hydroxides. In order to study the coprecipitation of germanium with the hydroxides of other metals as a function of the completeness of the precipitation of these hydroxides, we chose magnesium hydroxide (precipitation pH equal to, or about 11), manganese hydroxide (precipitation pH equal to, or about 9), and copper hydroxide (precipitation pH equal to, or about 5). The germanium concentration in the first two series of experiments was 180 μg in 50 ml, while in the experiments with $Cu(OH)_2$ it was 360 μg in 50 ml. The concentration of the metal in all the series was 25 mg in 50 ml. The hydroxides were precipitated with 0.2, 0.4, 0.6, 0.8, 0.9, and 1.0 equivalents of NaOH solution per equivalent of the corresponding metal. The results obtained are given in Table 6 and in Fig. 3.

It is clear that coprecipitation of germanium with the hydroxides of these metals differs essentially from coprecipitation of germanium with ferric hydroxide (Fig. 3). With magnesium and manganese hydroxides, quantitative extraction of germanium is achieved after adding only 0.2 equivalent of NaOH to one equivalent of metal, while with ferric hydroxide germanium is only extracted completely after adding all the requisite amount of alkali. Cupric hydroxide occupies an intermediate position between these extremes; in this case germanium is completely extracted on addition of about 60-70% of the equivalent amount. In our experiments with cupric hydroxide, the small decrease in completeness of germanium coprecipitation towards the end of precipitation of all the copper can be explained by partial dehydration of the hydroxide precipitate, which was observed during removal of the precipitate. It was established that germanium is also quantitatively coprecipitated with Al, Sn, Pb, Ti, and Bi hydroxides.

DISCUSSION OF RESULTS

Coprecipitation of germanium with ferric hydroxide is of very great importance for the extraction of small amounts of germanium from dilute solutions. Combined with subsequent distillation or extraction, this technique enables germanium to be freed from most of the impurities which interfere with its analytical determination. Magnesium and manganese hydroxides could also be used – less successfully – instead of ferric hydroxide.

As for the coprecipitation mechanism, the simplest explanation would be to assume formation of sparingly soluble metagermanates which are then entrained by the precipitate. The absence of coprecipitation during the beginning of the precipitation of $Fe(OH)_3$ and $Cu(OH)_3$ cannot, however, be explained on the basis of this assumption; it is known that ions of metagermanic acid predominate in solution at even lower pH values than those at which the hydroxides indicated are precipitated. It is also difficult to explain the insignificant coprecipitation of germanium with $MgNH_4PO_4$ which we established. In addition, it must be assumed that the low solubility of metagermanates is not a probable factor.

It is clear from the experimental results obtained that germanium is coprecipitated with the hydroxides of very many metals, but that quantitative coprecipitation only occurs at pH values which are higher than a certain limit (about six). For solving the question of the mechanism of coprecipitation, which, of course, requires further special investigation it is evident that in order to explain this mechanism it is necessary to look into: 1) The general structural characteristics of sparingly soluble hydroxides, and 2) general changes in the anionic forms of germanium in solution.

We should like to thank A. V. Moskvin for his valuable advice.

SUMMARY

Coprecipitation of germanium with ferric hydroxide is a valuable technique in analytical practice for the quantitative extraction of germanium from dilute solutions.

It is very difficult to wash out the germanium from the ferric hydroxide precipitate with water and ammonia, but quantitative extraction is possible with sodium sulfide solution.

High concentrations of common chlorides and nitrates do not interfere with quantitative extraction of germanium.

The coprecipitation process is reversible.

Germanium is also quantitatively coprecipitated with the hydroxides of a number of other metals; of these magnesium and manganese hydroxides could find practical application.

Some data have been obtained on the mechanism of coprecipitation.

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THIOMALIC ACID AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF MOLYBDENUM

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There are published references [1, 2] to the fact that during the interaction of thiomalic acid (mercaptosuccinic) acid HOOC·CH_2·CHSH × COOH with molybdate in a weakly acid (pH about 4.5), or acid (0.3 N H_2SO_4) medium, a yellow colored compound is formed. The sensitivity with which sexivalent molybdenum can be detected when th s reaction is carried out in a test tube or by a spot technique is fairly high [1]. Sexivalent tungsten does not give a color [2]. The ions of a number of other elements form soluble colored compounds or precipitates under various conditions [1, 2]. Thiomalic acid has been suggested as a reagent for detecting palladium [3].

Among the aims of the work described here was a study of the reaction between sexi- and quinquevalent molybdenum and thiomalic acid, and establishment of the possibility of carrying out a quantitative photometric determination of molybdenum by means of this reagent. The interaction of molybdenum with thioglycolic acid has been studied in the same way [4].

EXPERIMENTAL

Thiomalic acid was synthesized by interaction of maleic acid with excess sodium hydrosulfide [5]. After three recrystallizations from diethyl ether, the thiomalic acid prepared had a melting point of 146-147° (published figure, 149-150°). The SH content of the product obtained, as determined by the method of Obtemperenskaya, Terent'ev, and Buzlanova* [6], was 21.92, 22.19, and 22.08% (theoretical value 22.05% SH). It should be pointed out that the reagent used for the photometric determination of molybdenum need not be subjected to such careful purification.

Thiomalic acid is a white crystalline material which is readily soluble in water. It is completely stable in air, does not possess a disagreeable odor, has reducing properties, and is readily oxidized by iodine solution

Solutions of thiomalic acid were prepared by dissolving accurately weighed aliquots of the carefully purified preparation in water. Their concentrations were determined by titration with alkali solution using a glass electorde (the acid is dibasic), and iodometrically [7]; the latter method is based on oxidation of thiomalic acid with excess iodine solution in a strongly alkaline medium, followed by back titration of the iodine with thiosulfate solution, after acidification. All the remaining solutions and apparatus used were the same as those described previously.

Valence of Molybdenum in its Compounds with Thiomalic Acid. Under certain conditions, thiomalic acid forms colored compounds with molybdenum in its quinque- and sexivalent states.

Trivalent molybdenum (in the form of weak hydrochloric acid solutions of $(NH_4)_2MoCl_5$) does not give characteristically colored compounds with thiomalic acid at pH 1-4.

* The determinations were carried out by M. M. Buzlanova whom the authors wish to thank.

Quinquevalent molybdenum as $(NH_4)_2MoOCl_5$, at acidities varying from 0.5 M HCl to pH 7, interacts with thiomalic acid, a yellow color being formed. At pH > 7 the color intensity decreases, and at pH > 9 the solution becomes colorless. When such a solution is acidified to pH 3-5 a yellow color reappears. Excess thiomalic acid prevents hydrolysis of quinquevalent molybdenum when the pH is increased; the solution remains colorless.

Sexivalent molybdenum reacts with thiomalic acid at pH 2-5. A greenish-yellow color appears almost instantaneously, and it is stable in air when excess thiomalic acid is present. The valence of molybdenum at pH 3-6 does not change in the presence of excess thiomalic acid (see below), although the latter possesses clearly evident reducing properties. On adding the minimum amount of thiomalic acid to 0.1 M molybdate solution (pH 4) a yellow color is formed which is unstable, and after 5-10 min changes into the blue (molybdenum blue is formed).

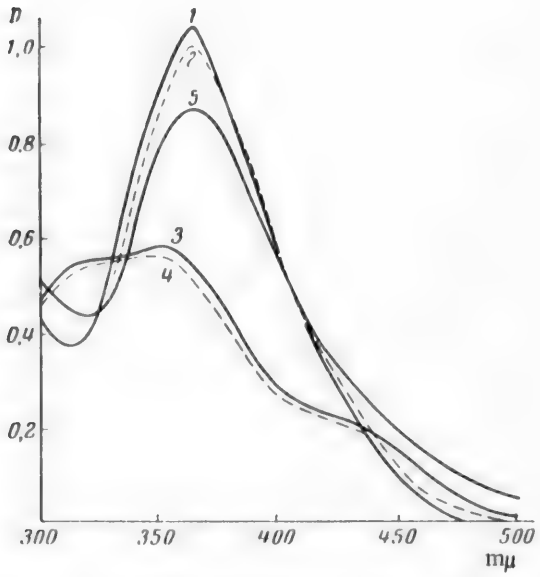


Fig. 1. Absorption curves for solution of the compounds of sexi- and quinquevalent molybdenum with thiomalic acid at various pH's. 1) Sexivalent molybdenum compound at pH 3.52; 2) sexivalent molybdenum compound obtained by mixing solutions of $(NH_4)_2MoOCl_5$ and thiomalic acid at pH > 10, after standing for several minutes (oxidation of Mo^V to Mo^{VI}) the pH was then adjusted to 4.58; 3) quinquevalent molybdenum compound at pH 1.48; 4) sexivalent molybdenum compound obtained by mixing solutions of molybdate and thiomalic acid and adjusting the pH to 0.68; 5) quinquevalent molybdenum compound at pH 5.52. In all cases [Mo] = 2.0×10^{-4} M; [RSH] = 0.02 M; l = 1 cm. The optical density was measured relative to water.

Photometric Characteristics of the Compounds of Sexi- and Quinquevalent Molybdenum with Thiomalic Acid. Absorption curves for solutions of the compounds of sexi- and quinquevalent molybdenum with thiomalic acid (Fig. 1) were obtained as follows: To 2.5 ml of a 2×10^{-3} M sodium molybdate solution or a solution of a salt of quinquevalent molybdenum in 1 M HCl, contained in a 25 ml standard flask, was added 10 ml of water and 5 ml of 0.1 M thiomalic acid with a pH of 4-5; the acidity of the solution was adjusted to a definite value by careful dropwise addition of sodium hydroxide or hydrochloric acid solutions with efficient stirring. During this process it is necessary to avoid local increases in acid or alkali concentration. When more than the requisite amount of acid (or alkali) was added, the solution was discarded. Only by observing these precautions is it possible to avoid premature partial reduction of sexivalent molybdenum at low pH values, and oxidation of quinquevalent molybdenum at high pH values. Afterwards the solution was diluted to the mark and the pH measured with a glass electrode. A solution of the compound of quinquevalent molybdenum with thiomalic acid with a pH of 5.52 was obtained by adding an acetate buffer solution with a pH of 7. Since thiomalic acid solutions do not absorb light in the 300-700 mμ region, the optical density was measured with respect to water on a SF-4 spectrophotometer in a cuvette with a layer thickness of 1 cm*.

The absorption curve of solutions of the compound of sexivalent molybdenum with thiomalic acid at pH 3.52 has a maximum at 365 mμ (Fig. 1, Curve 1). The absorption curve of solutions of the compound of quinquevalent molybdenum with thiomalic acid at pH 1.48 has a maximum at 352.5 mμ. The absorption curves of solutions of the compounds of sexivalent and quinquevalent molybdenum with thiomalic acid are similar to the absorption curves of the corresponding compounds of molybdenum with thioglycolic acid for solutions with the same pH values [4].

During determination of the molar extinction coefficients of solutions of the compounds of sexivalent and quinquevalent molybdenum with thiomalic acid at various pH's, the optical density was measured at 365 mμ

* The disulfide, as well as molybdate, hardly absorbs any light in the 300-700 mμ region.

TABLE 1

Molar Extinction Coefficients of the Compounds of Sexi- and Quinquevalent Molybdenum with Thiomalic Acid (Concentrations, 2.0×10^{-4} M Mo^{VI} or Mo^{V} and 0.02 M thiomalic acid; layer thickness 1 cm)

Mo valence	D^{365}	ε_M^{365}	Acidity
Mo^{VI}	1,05	5250	pH 4,47
	1,05	5250	pH 4,04
	0,532 *	2660	0,3 *N* HCl
	0,523 *	2610	0,6 *N* HCl
Mo^{V}	0,510	2550	pH 1,26
	0,538	2690	pH 1,48
	0,518	2590	pH 1,55
	0,890	4450	pH 5,52
	0,950	4250	pH 5,50

* The final thiomalic acid concentration was 0.06 M; the optical density was measured 20 min after preparing the solution. At this acidity sexivalent molybdenum is reduced to the quinquevalent state.

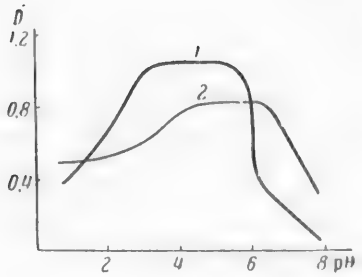


Fig. 2. Effect of pH on the optical density of solutions of the compounds of sexi- and quinquevalent molybdenum with thiomalic acid. [Mo]= $= 2.0 \cdot 10^{-4}$; [RSH] = 0.02 M. 1) Solution with sexivalent molybdenum- 2) solution with quinquevalent molybdenum.

in the presence of a large excess of thiomalic acid. The molar extinction coefficients (Table 1) were calculated with respect to the molar concentration of molybdenum.

Acidity Limits Within Which the Compounds of Sexi- and Quinquevalent Molybdenum with Thiomalic Acid Exist. The solutions used for establishing the acidity limits within which the compounds of sexi- and quinquevalent molybdenum with thiomalic acid exist were 2×10^{-4} M relative to sodium molybdate or to a salt of quinquevalent molybdenum in 1 N HCl, and 0.02 M relative to thiomalic acid. The pH of the solution was adjusted to the requisite value very carefully. In the case of quinquevalent molybdenum the pH of the solution was adjusted by addition of an acetate buffer solution with varying pH values, with careful stirring; the pH was finally measured with a glass electrode. The optical density was measured at 365 mμ relative to water, one hour after the pH had been determined (when the optical density had become constant).

The thiomalate of sexivalent molybdenum exists within the pH range 2 to 6; the optimum optical density is observed at pH 3-5 (Fig. 2). On increasing the pH from 6 to 8, the intensity of the greenish-yellow color rapidly decreases. There is a decrease in optical density below pH 3 also, presumably as a result of the reduction of sexivalent molybdenum with thiomalic acid, and the formation of the compound of quinquevalent molybdenum with thiomalic acid which has a relatively less intense yellow color.

Absorption curves for solutions of a mixture of sexivalent molybdenum and a large excess of thiomalic acid at pH 0.68, after standing for a long time, and for solutions of a mixture of a quinquevalent molybdenum salt with thiomalic acid at pH 1.48, almost coincide (Fig. 1, Curves 4 and 3; the molar molybdenum concentration in both cases was the same). This shows that at pH 0.68, sexivalent molybdenum is reduced to the quinquevalent state by thiomalic acid, and forms a yellow colored compound with excess of the latter. This conclusion is also confirmed by the coincidence observed between the calculated molar extinction coefficients of solutions obtained by mixing a salt of sexivalent molybdenum with thiomalic acid at a concentration of 0.3-0.6 N HCl, and of solutions of the compound of quinquevalent molybdenum and thiomalic acid at pH 1.48 (Table 1.).

The compound of quinquevalent molybdenum with thiomalic acid is stable at acidities ranging from 0.3 M to pH 7.5. The maximum optical density is observed at pH 4.5-6.5. On increasing the pH to 10 upwards, the solutions of the compound of quinquevalent molybdenum with thiomalic acid remain clear in the presence of excess of the latter. When the solution thereby obtained is carefully acidified with hydrochloric acid to a pH of 3-5, a greenish-yellow color appears (in contrast to the yellow color of the quinquevalent molybdenum compound at this same pH), the molar extinction coefficient being 5050. The absorption curve of the compound of sexivalent molybdenum with thiomalic acid at the same molar concentration (Curve 1, Fig. 1); these results show that quinquevalent molybdenum is oxidized to the sexivalent state by atmospheric oxygen or by water ions in the alkaline medium, even in the presence of excess thiomalic acid.

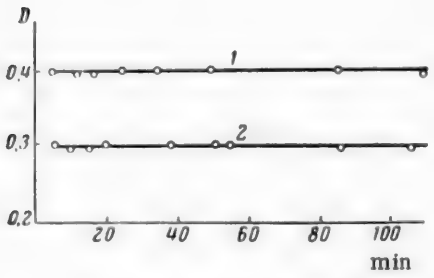
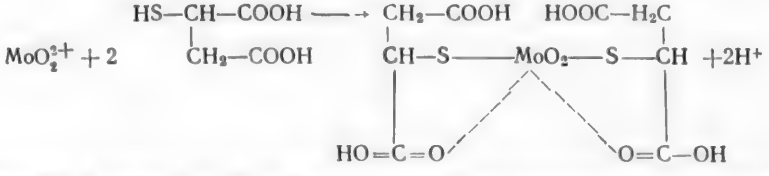


Fig. 3. The relation between the optical density of solutions of the compounds of sexi- and quinquevalent molybdenum with thiomalic acid, and time. The concentration of the sexi- and quinquevalent molybdenum was the same and equal to 8×10^{-5} M; thiomalic acid concentration 8×10^{-3} M; pH 3.6. 1) Compound of sexivalent molybdenum; 2) quinquevalent molybdenum compound.

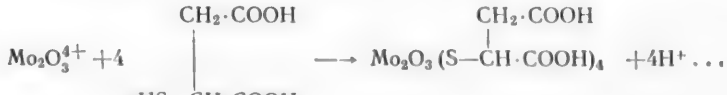
The compounds of molybdenum in the sexi- and quinquevalent state are almost stable with time at pH 3.6 in the presence of excess thiomalic acid (Fig. 3); reduction of sexivalent or oxidation of quinquevalent molybdenum does not occur.

The Composition of the Compounds of Sexi- and Quinquevalent Molybdenum with Thiomalic Acid. The molar ratios in which sexi- and quinquevalent molybdenum interact with thiomalic acid were established by the isomolar series methods. Different volumes of a 0.02 M solution of sodium molybdate or of a quinquevalent molybdenum salt (in 1 N HCl) were mixed with an almost neutral 0.02 M solution of thiomalic acid, so that the sum of the molar concentrations of both components in the final solution (after dilution) was always 9.6×10^{-4} M. The acidity of the solutions was adjusted by addition of 5 ml of an acetate buffer with pH 3.6 (in the case of sexivalent molybdenum) or by the calculated amount of hydrochloric acid until its concentration was 0.04 N HCl (in the case of quinquevalent and sexivalent molybdenum). Sexivalent molybdenum interacts with thiomalic acid at pH 3.6 almost instantaneously; the optical density was measured not later than 20 min after preparing the solutions. On standing for a longer time, some of the solutions containing excess sexivalent molybdenum turned blue. Solutions in 0.04 N HCl were prepared as follows: after mixing the solutions of the molybdenum salt, thiomalic acid, and the requisite amounts of hydrochloric acid, the final solution obtained was immediately diluted with water to the mark; the hydrochloric acid concentration was 0.04 N (taking into account the hydrochloric acid in the original solution). In order to attain equilibrium, in the case of sexivalent molybdenum, the solutions were allowed to stand for three hours, while in the case of quinquevalent molybdenum they were allowed to stand one hour. The optical density of solutions of the compound of quinquevalent molybdenum with thiomalic acid was measured relative to solutions of a quinquevalent molybdenum salt of equal molar concentration and of the same pH, but not containing thiomalic acid.

It is clear from Fig. 4 that the maximum optical density of solutions at pH 3.6 is observed at a molar ratio of sexivalent molybdenum to thiomalic acid of 1 : 2. The reaction probably proceeds as follows:



It is clear from Fig. 5 that in 0.04 N HCl, quinquevalent molybdenum also reacts with thiomalic acid in the molar ratio of 1 : 2. This leads one to suggest that in 0.04 N HCl the reaction proceeds according to the following equation:



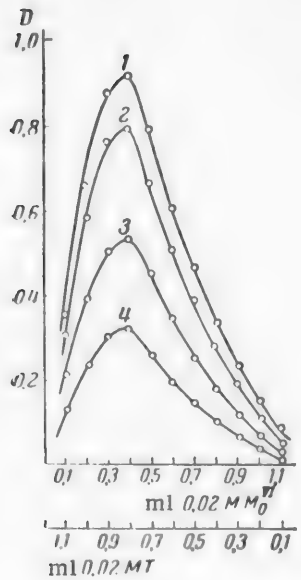


Fig. 4. Interaction of sexivalent molybdenum and thiomalic acid at pH 3.6; the optical density was measured relative to water. 1) At 360 mμ; 2) at 380 mμ; 3) at 400 mμ; 4) at 420 mμ.

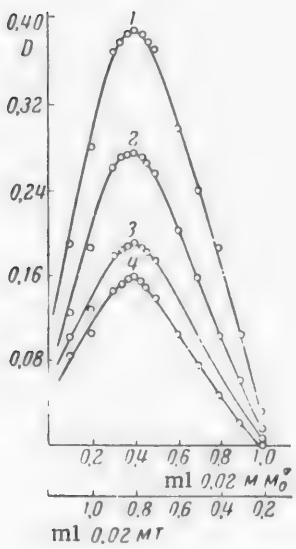


Fig. 5. Interaction of quinquevalent molybdenum and thiomalic acid in 0.04 N HCl; the optical density was measured relative to solutions of a quinquevalent molybdenum salt with equal molar concentration in 0.04 N HCl. 1) At 350 mμ; 2) at 380 mμ; 3) at 400 mμ; 4) at 420 mμ.

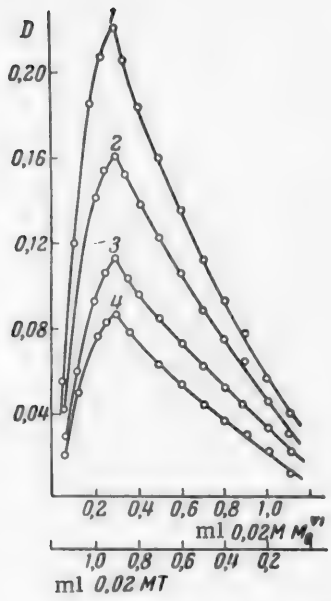


Fig. 6. Interaction of sexivalent molybdenum with thiomalic acid in 0.04 N HCl; the optical density was measured relative to water. 1) at 350 mμ; 2) at 380 mμ; 3) at 400 mμ; 4) at 420 mμ.

The maximum optical density in experiments with sexivalent molybdenum in 0.04 N HCl is found at a molar ratio of molybdenum to thiomalic acid of 1 : 3 (Fig. 6), i. e., one mole of molybdate corresponds to three moles of thiomalic acid. The results obtained show that during the interaction of sexivalent molybdenum in 0.04 N HCl, one mole of thiomalic acid is used up in reducing the molybdate to the quinquevalent state; subsequently two moles of thiomalic acid react with one mole of quinquevalent molybdenum. Similar results were obtained during a study of the interaction of sexi- and quinquevalent molybdenum with thioglycolic acid [4].

Experiments on electrophoresis showed that the yellow colored compound of sexivalent molybdenum at pH 5.1, and that of quinquevalent molybdenum in 0.2 N HCl move toward the anode, i. e., thiomalic acid forms colored anionic complexes with molybdenum.

Photometric Determination of Mo with Thiomalic Acid in a 0.5 N Hydrochloric Acid Medium. As shown above, when a large excess of thiomalic acid is present in moderately acid solutions, the former completely reduces sexivalent molybdenum to its quinquevalent state, which then reacts with excess reagent to give a fairly intense yellow color. In 0.3-0.6 N HCl the optimum density is obtained 20 min after preparing the solutions, and thereafter remains constant for at least one day. In order to get the maximum optical density for a solution with a concentration of 2×10^{-4} M molybdate in a medium of 0.5 N HCl, it is necessary to add more than 10 ml of 0.1 M thiomalic acid for a final volume of 25 ml. In 0.3-0.6 N HCl most accompanying elements do not form colored compounds with thiomalic acid.

A calibration curve is obtained as follows. Twelve ml of a standard solution of sodium molybdate containing not more than 1 mg molybdenum is placed in a 25 ml standard flask, and about 2 ml of dilute hydrochloric acid [1 : 1] is added; in this case the HCl concentration in the final solution will be 0.5 N. 7.5 ml of 0.2 M thiomalic acid solution is added and the solution diluted with water to the mark; it is then well mixed, and after 20 min the optical density is measured at 350, 365, 380, 400, or 420 mμ relative to water.

TABLE 2

Determination of Molybdenum in 0.5 M HCl in the Presence of Foreign Elements

Foreign elements, mg	Mo, mg			Foreign elements, mg	Mo, mg		
	taken	found	error		taken	found	error
Ti 37.3	0,50	0,53	+0,03	Ascorbic acid 500	0,60	0,61	+0,01
Zr 100	0,50	0,50	0	Thiourea 500	1,00	0,98	—0,02
Total rare earths 29.5	0,50	0,50	0	Fe 28,0 ($FeCl_3 \cdot 6H_2O$) **	0,30	0,32	+0,02
V 1,7	0,50	0,51	+0,01	Cu 1,3 ($CuSO_4 \cdot 5H_2O$) ***	1,00	1,01	+0,01
Cr 10,4	0,30	0,32	+0,02				
W 10,0 •	0,30	0,32	+0,02	Cu 3,2 ***	1,0	1,02	+0,02

• After filtering off the turbidity of H_2WO_4.

•• In the presence of 0.6 g ascorbic acid.

••• In the presence of 0.5 g thiourea.

TABLE 3

Determination of Molybdenum in the Presence of Foreign Elements at pH 3.6

Foreign elements, mg	Mo, mg			Foreign elements, mg	Mo, mg			Foreign elements, mg	Mo, mg		
	taken	found	error		taken	found	error		taken	found	error
Ba 2,75	0,77	0,79	+0,02	Mn 2,20	0,77	0,78	+0,01	Cu 2,79	0,77	0,41	—0,36
Mg 1,21	0,77	0,75	—0,02	Mn 2,75	0,77	0,74	—0,03	Cr 0,26	0,19	0,19	0,00
Ca 0,40	0,77	0,75	—0,02	V 0,26	0,77	0,79	+0,02	Cr 0,52	0,19	0,18	—0,01
Ca 1,60	0,77	0,80	+0,03	V 1,02	0,77	0,78	+0,01	Cr 0,52	0,19	0,18	—0,01
C 1,12	0,77	0,73	—0,04	Be 1,76	0,77	0,77	0,000	Cr 1,04	0,19	0,18	—0,01
Ni 1,17	0,77	0,78	+0,01	Al 1,30	0,77	0,30	—0,37	Cr 1,56	0,19	0,19	0,00
Zn 0,33	0,77	0,75	—0,02	Al 0,20	0,77	0,23	—0,54	Cr 2,60	0,19	0,17	—0,02

The solutions conform to Beer's law at concentrations from 1 to 40 μg Mo/ml.

Molybdenum was determined in synthetic mixtures using the same conditions but with the difference that the solution was neutralized first. The results obtained are given in Table 2. Large amounts of zirconium and titanium do not interfere in 0.5 N HCl. If hydrolysis products separate out during neutralization of the solution, on adding the requisite amount of hydrochloric acid and heating, the precipitate dissolves. Large amounts of trivalent iron do not interfere with the determination, if it is first reduced to the divalent state with ascorbic acid (the molybdate is also reduced to the quinquevalent state during this process). Vanadate is reduced by the reagent to the quadrivalent state, and gives a blue color which does not interfere with the determination. Tungstate does not give a color with the reagent, but in 0.5 N HCl a precipitate or suspension is formed. Separation of tungstic acid strongly affects the optical density, and accordingly it must be filtered off through a filter paper. Copper gives a yellow color with the reagent in 0.5 N HCl and interferes with molybdenum determination. Nevertheless, even large amounts of copper do not interfere when this element is complexed with excess thiourea. Large amounts of chromium and the rare earths do not interfere with molybdenum determination. In 0.5 N HCl a considerably smaller number of elements interfere with the determination of molybdenum than when the determination is carried out at pH 3-5, in 0.5 N HCl, however, the method is less sensitive.

Molybdenum can be determined in steels, or in alloys containing zirconium and titanium, by means of thiomalic acid. To 0.25 g of such an alloy is added 50 ml of HCl 1 : 1 and the mixture heated until complete so-

TABLE 4

Determination of Molybdenum in the Presence of Iron at pH 3.6 (0.77 mg Mo taken)

Fe added, mg	Mo found, mg	Mo error, mg
1,7	0,76	—0,01
2,8	0,77	+0,00
5,6	0,74	—0,03
5,6	0,71	—0,06
5,6	0,80	+0,03
11,2	0,77	+0,00
16,8	0,74	—0,03
22,0	0,78	+0,01
35,5	0,78	+0,01

lution has been effected; nitric acid is then added dropwise in order to oxidize trivalent titanium, and the solution quantitatively transferred to a 100 ml standard flask. An aliquot of this solution is taken for molybdenum determination, the operations described above (in 0.5 N HCl) being subsequently followed.

In an alloy containing 93.45% Ti and 1.47% Zr, the amount of Mo found was 4.38, 4.60, and 4.67%. Using the thiocyanate method, after chromatographic separation of molybdenum, assistant Mu Bin-Ven found 4.69, 4.63, and 4.69% Mo in the same alloy.

Photometric Determination of Molybdenum at pH 3.6. As already established, sexivalent molybdenum forms an intensely colored, completely stable yellow compound in weakly acid media in the presence of a large excess of thiomalic acid. The optimum optical density of the solutions is observed at pH 3-5. More than 10 mg of thiomalic acid is required for 1 mg Mo in order to get the optimum optical density. Since acetate ions do not lead to a drop in the optical density, an acetate buffer can be used for establishing the requisite acidity.

A calibration curve is constructed as follows: to 25 ml of an almost neutral solution of sodium molybdate of known concentration contained in a 50 ml flask, and containing not more than 1.2 mg Mo, is added 5-10 ml of acetate buffer and 3.0 ml of a 0.5% aqueous solution of thiomalic acid. The volume of the liquid is made up to the mark, mixed, and the optical density measured on a spectrophotometer in a cuvette with a layer thickness of 1 cm at 365 mμ relative to water. The solutions conform to Beer's law within the limits 1 to 40 μg Mo/ml.

TABLE 5

Determination of Molybdenum in the Presence of Tungsten (0.77 mg Mo taken)

W, mg	Mo, mg							
	360 mμ		380 mμ		400 mμ		420 mμ	
	found	error	found	error	found	error	found	error
1,0	0,87	+0,10	0,81	+0,04	0,78	+0,01	0,79	+0,02
5,0	0,86	+0,09	0,80	+0,03	0,75	—0,02	0,76	—0,01
6,0	0,87	+0,10	0,89	+0,03	0,75	—0,02	0,78	+0,01
10,0	0,94	+0,17	0,81	+0,04	0,71	—0,06	0,70	—0,07
10,0	0,94	+0,17	0,83	+0,06	0,74	—0,03	0,74	—0,03
10,0	0,94	+0,17	0,83	+0,06	0,77	+0,01	0,80	+0,03
15,0	0,94	+0,17	0,77	0,00	0,75	—0,02	0,75	—0,02
20,0	0,98	+0,21	0,83	+0,06	0,75	—0,02	0,75	—0,02

Determination of Molybdenum in the Presence of Foreign Elements at pH 3.6. Trivalent iron at pH 1-5 forms a blue colored, soluble compound with thiomalic acid. Nevertheless, the blue color of the solutions rapidly disappears, probably, because of the reduction of trivalent iron to the divalent state. Iron does not interfere with the determination of molybdenum. Tungsten does not give colored compounds with thiomalic acid. In the presence of this element, however, appearance of the colored molybdenum compound is delayed. The higher the tungsten concentration, the slower the rate at which the color develops. When not more than 5 mg of W is present, the optical density reaches its maximum value in half an hour, while in the presence of 5-20 mg of W, it takes 1-2 hours to reach its maximum value. It should be pointed out that the potassium tungstate solution itself absorbs only to a small extent at 300-400 mμ.

TABLE 6

Determination of Molybdenum in Steel

Aliquot No.	Standard sample No. 31-V, chromenickelmolybdenum steel* (0.27% Mo)		Standard sample No. 158 steel** (2.23% Mo)	
	found	error	found	error
1	0,25	−0,02	2,13	−0,10
	0,27	0	2,25	+0,02
	0,28	+0,01	2,21	−0,02
2	0,27	0	2,17	−0,06
	0,30	+0,03	2,34	+0,11

* Content of other elements (%) Mn_4 0.365; Si 0.275; S 0.017; P 0.023; Cr 1.24; Ni 3.40.

** Content of other elements (%) Mn_4 0.87; Si_4 0.70; S 0.008; P 0.032; Cr 13.18; Ni 12.71; Co 10.35; W 3.03; V 0.03; Nb 1.08.

Accordingly, the optical density must be measured at 400 mμ; in this case, however, the sensitivity of molybdenum determination decreases significantly. Ba, Mg, Ca, Ni, Cd, Zn, Mn, and Be do not interfere with molybdenum determination; vanadium gives a green-blue color with thiomalic acid, this color slowly disappears in the presence of excess reagent. Small amounts of vanadium do not interfere with molybdenum determination. Copper interferes with the determination, since it gives a cherry color with the reagent; aluminum interferes. Small amounts of chromium do not interfere, as long as the test solution is first acidified with hydrochloric acid, a small excess of reagent is added (10 ml of a 0.5% aqueous solution of reagent for 50 ml) and the solution finally neutralized by addition of alkali.

Results for the determination of molybdenum in the presence of foreign ions at pH 3.6 are given in Table 3. Cyanide and acetate anions do not interfere with molybdenum determination. Sodium ethylenediaminetetraacetate, oxalic acid, citric acid, and tartaric acid strongly depress the optical density of the solution and should be absent. Since CN^- ions do not interfere with molybdenum determination, it might be possible to determine molybdenum in the presence of copper after masking the latter with cyanide.

In order to determine molybdenum in the presence of iron, 0.5% aqueous thiomalic acid solution is added dropwise with continuous vigorous stirring to the acid solution (pH 1-2) containing Fe^{III} until the blue color ceases to appear. When large amounts of iron are present, a saturated thiomalic acid solution is added. Toward the end of this operation the reagent should be added slowly, and several seconds allowed to elapse between addition of each drop until the blue color has disappeared completely. A further 5 ml of the reagent is added, followed by alkali solution until a weakly acid or neutral reaction is given (a white turbidity sometimes appears during neutralization, but this disappears toward the end of the neutralization). 5-10 ml of acetate buffer is added (a violet color sometimes appears at this stage, but this disappears after a few minutes), and the volume of the solution made up to the mark, the solution is mixed, and after 15-30 min its optical density is measured relative to water when small amounts of iron are present (< 5 mg). When large amounts of iron are present, measurements are made relative to a solution containing approximately the same amount of iron, and which has been prepared in the same way. Results obtained are given in Table 4.

In order to determine molybdenum in the presence of tungsten, 5-10 ml of acetate buffer solution and 3.0 ml of 0.5% aqueous thiomalic acid solution are added to 25 ml of an almost neutral test solution containing not more than 1.2 mg Mo and not more than 20 mg W. After mixing, the solution is allowed to stand for 1-2 hr; it is then diluted to 50 ml, mixed, and its optical density measured at 400 mμ relative to water. Results for the determination of molybdenum in the presence of tungsten are given in Table 5.

Molybdenum is determined in steel at pH 3.6 by dissolving 1 g of steel in 20 ml HNO_3 (1 : 1) and 20 ml H_2SO_4 (1 : 1) in a 300 ml beaker, and evaporating the solution obtained to the appearance of white fumes.

When the steel does not dissolve completely, 20 ml of HCl (1 : 1) is added, and the solution evaporated to dryness; this operation is repeated several times. After cooling, 80 ml of water is added and the mixture heated until complete solution of the salts is attained. Silicic acid is filtered off on a filter paper, the filter plus residue are washed several times with water and the filtrates collected in a 200 ml flask; after cooling, the volume is made up to the mark with water. A few ml of the solution obtained is pipetted into a 50 ml flask and the solution prepared in the same way as that adopted for construction of the calibration curve; the optical density is measured on a spectrophotometer and the amount of molybdenum determined by means of the calibration curve. Results for the determination of molybdenum in standard samples of alloy steel Nos. 158 and 31-V are given in Table 6.

Thiomalic acid can be used for the photometric determination of molybdenum in the same way as thioglycolic acid. The advantage of thiomalic acid over thioglycolic acid is that the former is easier to handle, and has a lower tendency to be oxidized by atmospheric oxygen.

SUMMARY

The interaction of sexi- and quinquevalent molybdenum with thiomalic acid has been studied under various conditions. It has been shown that the reaction proceeds in a similar way to the reaction with thioglycolic acid.

Two variants have been developed for the photometric determination of small amounts of molybdenum (in a 0.5 N HCl medium and at pH 3.6). The selectivity of the method in a 0.5 N HCl medium is considerably higher than at pH 3.6, but the sensitivity is less.

The methods developed can be used for the determination of molybdenum in multialloyed steels.

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2,7-BIS-(4-CHLORO-2-PHOSPHONOBENZENEAZO)-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULFONIC ACID (CHLOROPHOSPHONAZO III), A NEW REAGENT FOR THE PHOTOMETRIC DETERMINATION OF URANIUM

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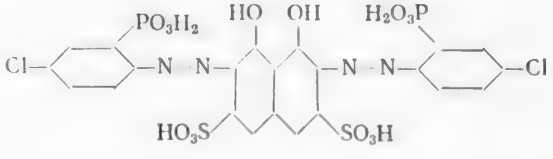
In a previous communication [1] we described a method for the photometric determination of sexivalent uranium by means of 2-(4-chloro-2-phosphonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (chlorophosphonazo I) which is the first organic color reagent containing the group PO_3H_2. The introduction of this group into the molecule of an organic reagent enables the reagent to interact with a number of cations in considerably stronger acid solution than is possible in the case of reagents with an analogous structure containing the groups AsO_3H_2, COOH, or OH instead of PO_3H_2. The synthesis and study of other representatives of this class of reagents is undoubtedly of considerable interest. The present article is devoted to the results of an analytical study of a new reagent which is a structural analog of arsenazo III, a reagent recently suggested by Savvin [2]; this new reagent is—2,7-bis-(4-chloro-2-phosphonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (chlorophosphonazo III), which we also studied from the point of view of its possible use for the photometric determination of sexivalent uranium.



Chlorophosphonazo III is readily soluble in water. Aqueous solutions at pH < 3 have a rose color. On increasing the pH to 3.0 the rose color acquires a violet tinge, while at pH 4 upwards it changes to violet. Solutions of chlorophosphonazo III in concentrated sulfuric and hydrochloric acids have a bright-green color. In concentrated nitric acid the bright-green color rapidly disappears as a result of oxidation of the reagent. In dilute nitric acid solutions (up to 3 N) chlorophosphonazo III possesses a stable rose color. Chlorophosphonazo III gives a greenish-blue color to solutions of sodium acetate and bicarbonate, a light-blue color to solutions of aluminum hydroxide and the carbonates of the alkali elements, and a blue color to solutions of the caustic alkalis.

Chlorophosphonazo III reacts with the ions of many elements in acid solutions. In the presence of Al^{3+}, Cu^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Tl^{+}, VO^{2+} and the rare earths, the rose color of solutions of the reagent changes

to pale blue, while in the presence of Ba^{2+}, Sr^{2+}, Ca^{2+}, Be^{2+}, Ni^{2+} and Pb^{2+} it becomes turquoise. During the reaction with Cr^{III} salts the turquoise color appears gradually, and only develops to its fullest extent after 15-20 min (on heating, this color change from rose to turquoise is completed appreciably more quickly).

The color change with the greatest contrast is observed in the presence of Ce^{IV}, Ti^{IV}, Zr, Hf, Th, U^{VI} and U^{IV}; the color change in these cases is from rose to green. Interaction of chlorophosphonazo III with other elements is not accompanied by an essential change in the color of the solutions of the reagent.

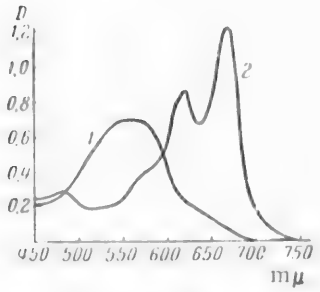


Fig. 1. Optical density of solutions of chlorophosphonazo III and of its compound with sexivalent uranium at pH 1.0. 1) 1.6×10^{-5} M solution of chlorophosphonazo III; 2) solution of the uranium compound containing 1.6×10^{-5} M chlorophosphonazo III and 7.6 mg U/ml. 10 mm cuvette.

It should be pointed out that the color reaction of chlorophosphonazo III with Ce^{IV}, Ti^{IV}, Zr, Hf, Th, U^{VI}, and U^{IV}, apart from its high contrast, possesses a very high sensitivity. The UO_2^{2+} ion is outstanding in this respect; it is the only doubly charged ion which forms a green colored compound with chlorophosphonazo III.

Absorption curves for solutions of chlorophosphonazo III and of its compound with sexivalent uranium are shown in Fig. 1. The maximum absorption of chlorophosphonazo III solutions is observed at 555 mμ, while the maximum absorption of solutions of the uranium compound are observed at 620 mμ and at 670 mμ. The absorption of the reagent in the region of the latter maximum is insignificant.

Compared with other reagents (including arsenazo III), chlorophosphonazo III reacts with sexivalent uranium in more acid solutions. From pH 4 and down to an acidity of about 0.5 N with respect to HCl, the absorption of solutions of the compound remains constant (Fig. 2). The independence of the absorption of the acidity means that uranium can be determined without establishing the pH carefully, and no special buffer solutions have to be used.

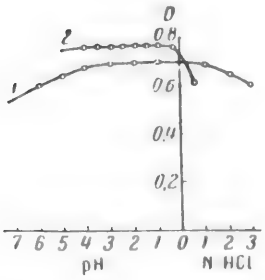


Fig. 2. Optical density of solutions of chlorophosphonazo III and of its compound with sexivalent uranium as a function of the acidity of the solution. 1) 1.6×10^{-5} M chlorophosphonazo III solution, wavelength 555 mμ, cuvette 10 mm; 2) solution of the compound (1.0×10^{-5} M with respect to uranium and 1.6×10^{-5} M with respect to chlorophosphonazo III), wavelength 670 mμ, cuvette 10 mm.

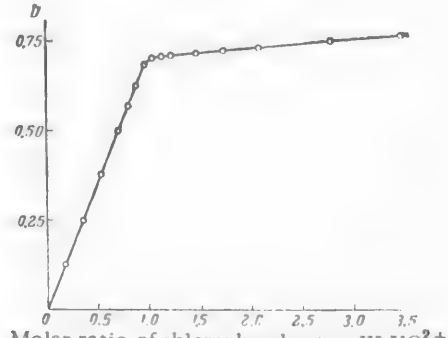


Fig. 3. Optical density of solutions with a constant concentration of sexivalent uranium and variable concentrations of chlorophosphonazo III. The uranium concentration was 0.780×10^{-5} M in all the solutions.

The optical density of the solutions reaches its maximum value immediately after the chlorophosphonazo III solution has been added, and does not change for more than 48 hr.

It was established by the isomolar series method that sexivalent uranium reacts with chlorophosphonazo III in the proportion of 1 : 1. The same

TABLE 1

Molar Extinction Coefficients of Solutions of the Compound of Sexivalent Uranium with Reagents Used for its Photometric Determination

Reagent	Molar extinction coefficient
Ammonium thiocyanate	3031 ± 26 [5]
Quercetin	12.800 [4]
Dibenzoylmethane	17.810*
Arsenazo I	22.800 [3]
1-(2-Pyridylazo)-2-naphthol	23.000 [6]
Chlorophosphonazo I	23.100 [1]
Arsenazo III	75.500*

* Calculated from the curve obtained during the photometric titration of a solution with a constant U^{VI} concentration.

TABLE 2

Interference from Foreign Elements during the Photometric Determination of U^{VI} by Means of Chlorophosphonazo

Interfering element	Permissible weight ratio of interfering element to uranium
Th, Zr, Hf, Ce^{IV}	0,05—0,1
Ti^{IV}	0,15
Bi, rare earths	0,2—0,3
Fe^{III}	0,35
Sn^{IV}	0,5
Pb	1
Cu, Nb, Ta, VO_2^{2+}	2—5
Ca, Sr, Ba, Be, Al	5—10
Fe^{II}	15
Cr^{III}	20
Zn, Ni, Hg^{II},	75—100
Tl^{III}	150
Co, Cd, Mu^{II}, Mg, Sb^{III}	200—250

result was obtained by the method of photometric titration in which the concentration of sexivalent uranium was kept constant and that of the chlorophosphonazo III was varied (Fig. 3). The sharp break on the curves indicates that the compound formed possesses a high stability.

The fact that there was only one break on the curves obtained during photometric titration, both when the concentration of sexivalent uranium was kept constant and that of chlorophosphonazo III was varied, and when the concentration of chlorophosphonazo III was kept constant while that of sexivalent uranium was varied, shows that, apart from the complex in which the ratio of reagent to uranium is equal to 1 : 1, no complexes with other compositions are formed.

The molar extinction coefficient, calculated from the photometric titration curve (Fig. 3), proved to be 78,600. Only with arsenazo III does sexivalent uranium form a compound, the molar extinction coefficient of which has approximately the same value as that of the complex with chlorophosphonazo III (Table 1).

The main advantage of chlorophosphonazo III as a reagent for the photometric determination of sexivalent uranium, as compared with other reagents, is the insignificant, and sometimes complete absence of any interference from masking agents. Chlorophosphonazo III is better in this respect than the reagent arsenazo III suggested recently by Savrin [2]. Thus, when arsenazo III (taken in double the amount required for the formation of a complex) is used for the determination of 48.75 μg of uranium in a final volume of 50 ml, at pH 1.75, the presence of 2.5 mg of sodium ethylenediaminetetracetate (EDTA-Na) appreciably interferes with the determination, while no interference on the part of EDTA-Na could be observed during the determination of uranium by means of chlorophosphonazo III under the same conditions, even when 100 mg of EDTA-A was present. Sodium tartrate does not interfere with the determination of uranium by means of chlorophosphonazo III, while 50 mg of sodium tartrate leads to a decrease of more than 5% in the optical density when uranium is determined by means of arsenazo III.

Chlorophosphonazo III can be used for the determination of sexivalent uranium in the presence of 50 times its amount of fluorides (calculated as NaF) and 5000 times its amount of phosphates (calculated as NaH_2PO_4). The masking agents indicated interfere to a greater extent when arsenazo III is used under the same conditions; the permissible amounts of oxalates, fluorides and phosphates are 2,5-3 times less in this case.

As indicated above, chlorophosphonazo III reacts with many elements; nevertheless, on increasing the acidity of the solutions, the interaction of the reagent with some of these elements is reduced or ceases altogether. Thus, while cobalt, nickel, cadmium, manganese, and zinc react at pH 3.0 with chlorophosphonazo to form intensely colored compounds, at pH 1 only appreciable amounts of these elements give rise to an observable change in the color of the reagent.

TABLE 3

Determination of Uranium in Synthetic Mixtures of Uranium and Zirconium

Taken, mg		U found, mg	Relative experimental error for uranium, %
U	Zr		
25,6	74,4	26,1	+2,0
27,2	72,8	26,9	—1,1
30,7	69,3	30,2	—1,6
42,4	57,6	43,1	+1,6
48,5	51,5	48,2	—0,6

Table 3 contains the permissible ratios by weight of a number of elements with respect to uranium, when the solution whose color is being measured has a pH of 1, and whose uranium content is 1.0 μg/ml while the total reagent concentration is 1.75×10^{-5} M.

Th, Zr, Hf, Ce^{IV}, and Ti^{IV} interfere to the greatest extent. Nevertheless, even in these cases, sexivalent uranium can be determined in the presence of significantly greater amounts of these elements, as long as suitable masking agents are used (e. g., NH_4F for masking Zr and Hf, and H_2O_2 for Ti^{IV}) or these elements are reduced beforehand to their lower valence states (e. g., Ce^{IV} to Ce^{III}, Fe^{III} to Fe^{II}, and Sn^{IV} to Sn^{II}).

Photometric Determination of Uranium in its Alloys with Zirconium. 100 mg of the test alloy is dissolved in a platinum basin in 10 ml of dilute hydrochloric acid (1 : 1), 0.5 g of NH_4F (or the equivalent amount of NaF or HF) being added while the basin is heated on a water bath. The time taken for a sample to dissolve does not exceed 5 min even when the sample has only been roughly ground. When dissolution is complete, 20 ml of 0.1 M Na_2SiO_3 is added to complex the HF (to prevent damage to the glass vessel), and the solution transferred to a 250 ml standard flask, the basin is rinsed with 10-15 ml of dilute hydrochloric acid (1 : 1) and the washings combined with the main solution. After dilution to the mark with water, 1.00 ml of the solution obtained is transferred to a 100 ml standard flask, 5.0 ml of a monochloroacetate buffer solution is added (10 g $ClCH_2COONa$ and 20 g of $ClCH_2COOH$ in 1 liter of solution), followed by 2.5 ml of 0.1 M Na_2SiO_3 solution, 12.5 ml of 0.1 M NH_4F (or NaF) solution, and 2.00 ml of 0.001 M chlorophosphonazo III solution; the volume is made up to the mark with water and the optical density of the solution obtained is measured on a spectrophotometer in a cuvette with a layer thickness of 10 mm, at 670 mμ. The reference solution used is a solution containing the same amounts of chloroacetate buffer, Na_2SiO_3, NH_4F, and reagent, but not containing uranium and zirconium. The uranium content is determined from a calibration curve.

A calibration curve is constructed by introducing various amounts of a standard uranyl nitrate solution (containing 50, 100, 150, 200, and 250 μg U) into 100 ml standard flasks; monochloroacetate buffer solution, Na_2SiO_3, NH_4F, and reagent solutions are then added in the same amounts as those added to the test solution.

The method has been checked on synthetic mixtures made from metallic uranium and zirconium (Table 3).

The error does not exceed 2%. One determination takes about 15 min.

Synthesis of Chlorophosphonazo III. To 4.55 g (0.022 mole) of 2-amino-5-chlorobenzenephosphonic acid is added 60 ml of water and 4 ml of concentrated hydrochloric acid, the mixture is cooled on the outside with ice to 0-7°, and 1.7 g of sodium nitrite dissolved in 10 ml water added dropwise with stirring. The solution of 2-diazo-5-chlorobenzene phosphonic acid obtained is added to 4.5 g (0.01 mole) of chromotropic acid dissolved in 50 ml of a 10% sodium hydroxide solution. The pH of the mixture is adjusted to about 9 and it is stirred for two hours, a solution of sodium hydroxide being added periodically in order to maintain the pH of the mixture within the limits 8-9. Concentrated hydrochloric acid is next added until the solution gives a strongly acid reaction to congo red paper; the product which separates out is filtered off, washed twice with 25% hydrochloric acid, and dissolved in 100 ml of 2% sodium hydroxide. The solution obtained is again acidified with concentrated hydrochloric acid until the solution gives a strongly acid reaction to congo red; the product which settles out is filtered off, washed twice with hydrochloric acid and dried at 80°. On increasing the drying temperature further

to 160° the weight of the product decreases by 8.75% as the result of loss of water of crystallization; the loss corresponds to four molecules of water per molecule of chlorophosphonazo III.

The product obtained is a crystalline powder with an intense dark-red, almost black color. It is readily soluble in water, and is insoluble in benzene, chloroform, CCl_4, and ether. It is slightly soluble in acetone and somewhat more soluble in ethanol.

Found %: P 8.32; Cl 9.38; N 7.29.
Calculated %: P 8.20; Cl 9.36; N 7.42.

SUMMARY

A new, highly sensitive reagent for the photometric determination of sexivalent uranium is suggested; the reagent has been designated chlorophosphonazo III. The molar extinction coefficient of solutions of the compound of uranium with this reagent is 78,600 at 670 mμ. The high stability of the colored compound formed enables sexivalent uranium to be determined in the presence of large amounts of fluorides, phosphates, and oxalates. Sulfates, tartrates, and ethylenediaminetetracetic acid do not interfere with the determination of uranium, however much of them are present. A method has been developed for the direct photometric determination of uranium in its alloys with zirconium, Na_2SiF_6 being used for eliminating interference from the zirconium.

The synthesis of chlorophosphonazo III is described.

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THE EFFECT OF VANADIUM ON THE DETERMINATION OF URANIUM BY THE HYDROSULFITE-PHOSPHATE TITRIMETRIC AND PHOTOMETRIC METHODS

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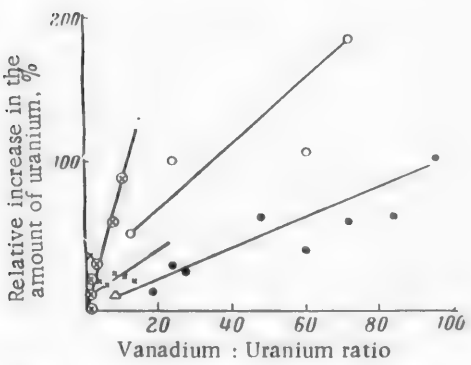
The titrimetric hydrosulfite-phosphate method of determining uranium was suggested by Volkov [1] and given a theoretical basis by Moiseev [1]. This method gives reliable results in many instances during the analysis of complex materials. Ponomarev [1] has developed a hydrosulfite-phosphate photometric method for the determination of small amounts of uranium.

During studies of the effect of various elements on the results of uranium determination by the titrimetric and photometric hydrosulfite-phosphate methods, it was found that vanadium leads to high results for uranium. As can be seen from Table 1, results of the titrimetric determination increase as a function of the relative amount of vanadium introduced by 10-85%; when the photometric variant is used the increase is doubled, reaching 190%. The higher the vanadium content, the greater the error. The absolute error also increases with increasing uranium content of the sample. In sample No. 2 which is poor in uranium, the relative error of the titrimetric error is about 50%, while in sample No. 1 which contains five times as much uranium, the relative error is 18-20%. The relative error is even smaller for samples containing 7% uranium.



The error in determining uranium as a function of the relative vanadium content of the sample.

This observation can be explained if one takes into account the quantitative ratio of uranium to vanadium in the test sample. The relation between the increase in the results for the uranium determination and the relative vanadium content in the original solution is shown in the diagram. Despite the large scatter of the experimental points, particularly at low uranium contents, there is nevertheless a general tendency for the results to increase with increases in the ratio V : U.

In order to make sure that the high results are not connected with the presence of vanadium, but also with the presence of uranium, the phosphates were precipitated in the presence of hydrosulfite from samples free from uranium, and from samples containing thorium instead of uranium. In all these experiments, vanadium was not observed to exert any influence, within the limits of experimental accuracy.

When the uranium is determined using a vanadometric finish, vanadium only interferes when it is present in the final solution in the trivalent state.

Vanadium was shown to be present in the phosphate precipitate experimentally.

TABLE 1

Results of the Determination of Uranium in Natural Samples as a Function of the Amount of Vanadium Introduced

Vanadium added	Sample No. 1				Sample No. 2				Sample No. 3	
	by the titrimetric method		by the photometric method		by the titrimetric method		by the photometric method		by the titrimetric method	
	found %	rel. dev., %	found %	rel. dev., %	found %	rel. dev., %	found, %	relative deviation %	found, %	relative deviation, %
0,0	0,609	0,0	0,610	0,0	0,083	0,0	0,081	0,0	6,95	0,0
10,0	0,651	7,0	0,736	21,0	0,089	9,9	0,133	52,0	—	—
20,0	0,696	14,3	0,800	30,0	0,101	21,7	0,162	100,0	—	—
30,0	0,693	13,6	—	—	0,093	14,8	—	—	7,50	8,0
40,0	0,699	14,8	0,968	59,0	0,124	53,1	0,165	103,0	—	—
50,0	0,730	19,8	—	—	0,103	27,2	—	—	—	—
60,0	0,721	18,4	1,169	92,0	0,120	48,1	0,235	191,0	7,66	10,2
70,0	0,716	15,5	—	—	0,123	51,3	—	—	—	—
80,0	0,738	21,2	—	—	0,150	85,2	—	—	—	—
90,0	—	—	—	—	—	—	—	—	8,38	19,9

TABLE 2

Calculation of the Values of the Oxidation–Reduction Potentials in the System V^V/V^{IV} as a Function of the Acidity and the Concentration Ratios of the Vanadium Ions

pH	Oxidation-reduction potential		
	V^V/V^{IV}	V^V/V^{IV} 1/10	V^V/V^{IV} 1/100
0	+1,0	+0,942	+0,884
1	+0,884	+0,826	+0,768
2	+0,768	+0,710	+0,652
3	+0,652	+0,594	+0,536
4	+0,536	+0,478	+0,420
5	+0,420	+0,362	+0,304
6	+0,304	+0,246	+0,178

TABLE 3

Effect of pH of the Solution on Oxidation of Quadrivalent Vanadium Ions by Ferric Ions

Established pH of the solution	External appearance of the solution	Optical density	Note
1.7	Light-rose	0.11	Clear solution
2.0	Rose	0.21	Ditto
3.0	Red	0.67	" "
5.0	Red, turbid	?	Turbid filtrate
7.4	Ditto	0.74	Clear filtrate
9.0	" "	0.70	Ditto

X-ray structural studies of precipitates of uranium phosphates separated from solutions free from, and containing vanadium, showed that no new crystalline phase is formed. The fact that the x-ray spectrograms were completely identical, coupled with the large difference in the ionic radii of U^{IV} and V^{III} excludes the phenomenon of isomorphism. It only remains to suggest the occurence of selective adsorption of trivalent vanadium compounds in an amorphous form on the surface of the phosphate precipitate of quadrivalent uranium. This assumption agrees with the fact which we have established, that it is possible to remove vanadium from the phosphate precipitate by means of a solution of an oxidizing agent (see below) which has a low redox potential.

A comparison of the normal oxidation–reduction potentials of an acid solution of hydrosulfite, and of solutions containing vanadium in its various oxidation forms, shows that quinque- and quadrivalent vanadium should be reduced by hydrosulfite in an acid medium to its trivalent state. This phenomenon should also occur in weakly acid solutions.

In order to calculate the standard potential of a system in which oxidation of hydrosulfite in an acid medium

TABLE 4

Results of Titrimetric Determination of Uranium after Washing the Phosphate Precipitate with Iodine

Uranium taken, mg	Uranium found after treating the phosphates of U^{IV} with iodine, mg	Absolute deviation, mg
0,5	0,49	—0,01
1,0	1,0	±0,00
2,0	1,94	—0,06
5,0	5,02	+0,02
7,0	7,00	±0,00

occurs, using the results for the free energy of the hydrosulfite ion, Latimer [3] used the following equation for the reaction: $HS_2O_4^- + H_2O = 2H_2SO_3 + H^+ + 2e$.

It is not difficult to show that, according to this equation, the relation between the oxidation potential and the pH of the solution should conform to the equation:

$$E = E_0 + \frac{0,058}{2} \lg \frac{[H_2SO_3]^2}{[HS_2O_4]} - 0,029\,pH,$$

where E_0 is the normal oxidation–reduction potential of the solution, and equal to 0.08 v [3].

For the reduction of quadrivalent vanadium $VO^{2+} + 2H^+ + e = V^{3+} + H_2O$ the relation between the oxidation–potential and pH is of the form:

$$E = E_0 + 0,058 \lg \frac{[VO^{2+}]}{[V^{3+}]} - 0,116\,pH,$$

where E_0 is the normal oxidation–reduction potential, and is equal to 0.361 v [3].

Using the relationships indicated, it is possible to calculate the pH value, at which the hydrosulfite will not reduce the V^{IV} ions further; this is known to occur only when the oxidation–reduction potentials of both systems become equal to one another, i. e., E = E.

In order to be able to use the values of the normal oxidation–reduction potentials directly, it was arbitrarily assumed that the ratio of the concentrations of the oxidized to the reduced forms in the test solution is equal to unity, i. e.,

$$\frac{[VO^{2+}]}{[V^{3+}]} = 1 \qquad \frac{[H_2SO_3]^2}{[H_2SO_4^-]}$$

In this case the requisite pH will be equal to:

$$pH = \frac{E_0 - E_0}{0,116 - 0,029} = \frac{0,44}{0,087} = 5,06.$$

Thus, even in weakly acid solutions having a pH below 5, the quadrivalent vanadium ions should be reduced by more than 50% to the trivalent state by the hydrosulfite.

Since it has a low solubility, the phosphate of V^{III} separates out with the precipitate of uranium phosphate and sulfur, and thereby increases the titration results (see Table 1). When such a precipitate is washed on the filter with the "normal" wash liquor, the vanadium compound is not completely removed from it.

Vanadium interferes to an even greater extent during the photometric determination of uranium.

This observation led us to look for the reasons for the high results, not only in the reducing action of trivalent, but also in that of quadrivalent vanadium.

The main oxidation–reduction process in the photometric variant of the method is expressed by the equation: $U^{VI} + 2Fe^{III} = U^{VI} + 2Fe^{II}$.

Trivalent vanadium ions present in solution increase the concentration of ferrous ions according to the euqation: $V^{III} + Fe^{III} = V^{IV} + Fe^{II}$.

There is no doubt that oxidation of trivalent vanadium by ferric ions occurs, since the normal oxidation–reduction potential of the system V^{IV}/V^{III} is considerably lower than the potential of Fe^{III}/Fe^{II}. It is usually

TABLE 5

Effect of Washing the Phosphate Precipitates with Iodine Solution on the Vanadium Content of these Precipitates (6.1 mg U + 50 mg V)

Washing			
with iodine solution		water	
Vanadium found, mg			
in the precipitate	in the filtrate	in the precipitate	in the filtrate
0,0	0,480	0,336	0,0
0,0	0,154	0,160	0,0
0,0	0,154	0,112	0,0

accepted that in acid media, oxidation of vanadium is limited by the formation of quadrivalent vanadium ions. In order to explain this, we were compelled to assume that under the conditions used in the analysis, on switching over from strongly acid to neutral solutions the following process occurs: $V^{IV} + Fe^{III} = V^{V} + Fe^{II}$, which, according to [5], proceeds quantitatively in weakly alkaline and alkaline media.

That this process can, theoretically, occur, follows from an examination of the relationship between the oxidation–reduction potential of V^{V}/V^{IV} and the acidity of the solution. Actually:

$$2H_2O + VO^{2+} \rightleftarrows V(OH)^{+} + 2H^{+} + e$$

$$\pi = \pi_0 + 0{,}058 \lg \frac{[V(OH_4)^{+}]}{[VO^{2+}]} - 0{,}116\ pH,$$

where π_0 is the normal oxidation–reduction potential equal to +1.0 v [3].

Table 2 contains the calculated values of the oxidation–reduction potentials of the system V^{V}/V^{IV} at various ratios of V^{V}/V^{IV} and various pH's of the solution.

By comparing the results given in Table 2 with the value of the normal oxidation–potential Fe^{III}/Fe^{II}, which is equal to +0.77 v, it is not difficult to see that under the most unfavorable conditions $V^{V}/V^{IV} = 1$, oxidation of quadrivalent vanadium to its quinquevalent state by ferric ions can occur even at pH 2. In those cases where quadrivalent vanadium ions predominate, oxidation may even be observed at pH 1. The possibility of oxidation increases when excess ferric ions are present, or when a material such as α,α'-dipyridyl is present, which can complex ferrous ions into a stable complex.

Oxidation of quadrivalent vanadium by ferric ions should be particularly marked at pH 2-4, since up to pH 4 (i. e., up to the beginning of hydrolysis of ferric iron) the value of the oxidation–reduction potential of Fe^{III}/Fe^{II} is almost independent of the pH.

The possibility of the oxidation of quadrivalent vanadium ions by ferric ions in a weakly acid medium was shown experimentally. A solution of the sulfate of quadrivalent vanadium containing 1 mg of vanadium was added to a decinormal solution of sulfuric acid; a sulfuric acid solution containing 5 mg of ferric iron was then added. The solutions, which had a volume of about 50 ml, were neutralized with tetraborate solution to a given pH value which was controlled by means of a pH-meter. To the solutions prepared in this way were added 2.5 ml lots of 0.5% α,α'-dipyridyl solution which interact with ferrous ions [4]. The optical density of the ferrodipyridyl solutions was measured on a FEK-M photocolorimeter.

Similar experiments were carried out in which no ferric salt solution was added; after addition of the α,α'-dipyridyl, all the solutions were colorless, showing thereby that α,α'-dipyridyl does not react with vanadium ions, and also showing the absence of ferrous ions; when a solution of ferrous iron was added, as a control, a color developed immediately.

Table 3 illustrates the reducing action of quadrivalent vanadium ions on ferric ions. Starting from pH 1.7 a rose color appears as a result of the formation of ferrous ions; this color almost reaches its limiting value at a pH as low as 3.

These experiments therefore demonstrate the reducing properties of quadrivalent vanadium with respect to ferric ions, not only in alkaline, but also in weakly acid media.

In order to eliminate interference from vanadium, it should be removed from the phosphate precipitate by washing the latter with a solution of oxidizing agent which is a weak one with respect to tri- and quadrivalent vanadium, and which will not affect the phosphate of quadrivalent uranium. As long ago as 1954 we suggested iodine solutions for this purpose.

TABLE 6

Results of Determination of Uranium in Natural Samples (With added Vanadium) after Washing the Phosphate Precipitates with Iodine Solution

Vanadium added, mg	Sample No. 1				Sample No. 2				Sample No. 3	
	found, %				found, %				found, %	
	titrimetrically		photometrically		titrimetrically		photometrically		titrimetrically	
	with iodine treatment	without iodine treatment	with iodine treatment	without iodine treatment	with iodine treatment	without iodine treatment	without iodine treatment	without iodine treatment	without iodine treatment	without iodine treatment
0,0	0,609	0,611	0,609	0,610	0,081	0,081	0,080	0,081	—	—
10,0	0,605	0,651	0,612	0,736	0,081	0,089	0,081	0,133	6,95	6,96
20,0	0,615	0,695	0,614	0,800	0,081	0,101	0,088	0,162	—	—
30,0	0,608	0,693	—	—	0,084	0,093	—	—	6,90	7,50
40,0	0,610	0,699	0,612	0,968	0,087	0,124	0,096	0,165	—	—
50,0	0,606	0,730	—	—	0,082	0,103	—	—	—	—
60,0	0,610	0,721	0,614	1,169	0,084	0,120	0,097	0,235	6,97	7,66
70,0	0,611	0,716	—	—	0,086	0,123	—	—	—	—
80,0	0,617	0,738	—	—	0,088	0,156	—	—	—	—
90,0	—	—	—	—	—	—	—	—	7,02	8,33

Oxidation of trivalent vanadium by iodine was carried out by additional washing of the phosphate precipitate on the filter.

The treatment of the precipitate with iodine solution also proved useful from another point of view, since iodine oxidizes any hydrosulfite decomposition products.

Table 4 contains results for the determination of uranium in synthetic solutions after the phosphate precipitate has been washed with iodine.

The following experiments were carried out in order to show that washing the phosphate precipitate with iodine solution leads to oxidation of any vanadium in this precipitate, and facilitates its removal. Equal amounts of uranium and vanadium, in two parallel samples, were treated under identical conditions with hydrosulfite, and were precipitated as their phosphates. The precipitates were transferred onto filters, and, as usual, were carefully washed with acidified water until the wash liquors gave a negative reaction with potassium permanganate. The first sample was then given an additional wash with an iodine solution having a pH of 5.

The second, parallel sample, was given an additional wash with the same volume of acidified water. Both of the precipitates on the filters, and both the filtrates obtained were analyzed for their vanadium content.

The results obtained (Table 5) leave no doubt regarding the removal of the vanadium from the precipitate.

The possibility of removing interference, even from large amounts of vanadium, during titrimetric and photometric determination of uranium, by washing the phosphate precipitate with iodine solution is illustrated by the results given in Table 6.

What was still not clear was the way the iodine eliminates interference from quadrivalent vanadium which may be formed as the result of incomplete oxidation of the trivalent vanadium contaminating the precipitate of quadrivalent uranium phosphate.

A comparison of the normal oxidation potential of iodine, equal to +0.536 v [3], with the potential of vanadium (Table 2) shows that at pH's above 4, iodine solutions should oxidize vanadium compounds to the quinquevalent state. The conclusion was confirmed experimentally.

Mixtures were prepared, each containing 1 mg V^{IV} + 50 ml water + 0.1 ml of a 0.1 N solution of iodine in potassium iodide + 2 ml of a 0.5% starch solution. All the reagents apart from the solution of a quadrivalent vanadium compound were used in parallel experiments. All the solutions had an intense blue color when the

mixtures were acid (pH 2-3.7). On adding sodium tetraborate to the solutions containing quadrivalent vanadium to adjust the pH to a definite value, it was found that the blue color disappeared at pH's above 4. Solutions which did not contain vanadium kept their blue color over the range pH 2.0-9.3.

Thus, as the quinquevalent vanadium compound is formed as the result of oxidation with iodine, it is washed out from the precipitate by the aqueous solution of iodine having a pH of 5.0-5.5.

The work carried out makes it possible to improve the titrimetric [6, 7] and the indirect photometric [2] methods of determining uranium in mineral raw material of complex composition.

SUMMARY

It has been shown that the high results obtained during the determination of uranium by the hydrosulfite-phosphate method when vanadium is present, can be ascribed to the adsorption of lower vanadium compounds by uranium (IV) phosphate.

It is suggested that interference on the part of vanadium can be eliminated by washing the phosphate precipitate with iodine solution.

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INTERACTION IN THE SYSTEM PALLADIUM-DIMETHYLGLYOXIME-TRIVALENT IRON

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Various oximes are widely used in the analytical chemistry of palladium for its gravimetric and photometric determination [1-4]. Many of these oximes permit palladium to be determined in the presence of a number of other elements, and to be separated from interfering elements. Nevertheless, ferric ions, when present in solution, often interfere with the completeness of the separation of palladium by oximes [5-7]. During the interaction of palladium ions with dimethylglyoxime in perchloric and nitric acid solutions, ferric ions, under certain conditions, can completely prevent formation of palladium dimethylglyoximate precipitate [8]. Under these conditions the solution has a dark-brown color. We have established earlier [9] that trivalent iron forms a soluble complex compound with dimethylglyoxime in acid media.

It might be assumed that in a solution containing palladium, dimethylglyoxime, and trivalent iron, interaction may occur with formation of a ternary compound.

Published information only relates to numerous attempts to decrease the influence of trivalent iron by masking the latter with various reagents. All these attempts, however, are purely empirical in nature, since there is no information on the composition of the ternary complex formed, its stability, and the stability limits, which is related to the latter.

We have tried to obtain the information which is lacking.

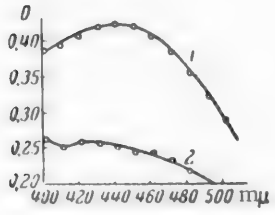


Fig. 1. Absorption curves of solutions of the ternary complexes for various ratios of $Pd : H_2Dm : Fe^{III}$. 1) $Pd : H_2Dm = 1 : 2$, Fe^{III} in excess; 2) $Pd : H_2Dm : Fe^{III} = 1 : 2 : 1$.

Optical density was measured on a SF-4 spectrophotometer. The hydrogen ion concentration was determined with a glass electrode.

The fact that the optical densities of the individual components of a solution containing simultaneously dimethylglyoxime, palladium and ferric ions are not additive confirmed our assumption to the formation of a ternary compound. In Fig. 1 (Curve 1) is shown the absorption curve of a solution in which $C_{Pd} = 9.5 \times 10^{-5}$ g·atom/liter, $C_{Fe^{III}} = 1.4 \times 10^{-3}$ g·atom/liter, $C_{H_2Dm} = 1.9 \times 10^{-4}$ M. The individual components of this solution, when taken separately, hardly absorb light at all at the given concentrations and pH, over the wavelength region examined.

In order to determine the composition of the compound formed in solution, it was necessary to combine various spectrophotometric methods.

The ratio between palladium and dimethylglyoxime was determined by the isomolar series method, the amount of trivalent iron being kept constant, and in a large excess with respect to palladium.

Fig. 2 illustrates the results obtained in experiments carried out at a wavelength of 440 mμ for two isomolar series with total concentrations of palladium ions and dimethylglyoxime of 8×10^{-5} M and 1.6×10^{-4} M, and a

pH of 2.10. The curves for the deviation of the measured optical densities from additivity have a maximum at a ratio of the components Pd : H_2Dm = 1 : 2. We obtained similar results in a series in which the total concentration of palladium and trivalent iron was kept constant while the dimethylglyoxime concentration was varied (Fig. 3). A hundredfold excess of trivalent iron was taken with respect to palladium, the pH was 2.23. The ratio Pd : H_2Dm was found to be 1 : 2; the optical density of the solutions did not change, starting at a twofold excess of dimethylglyoxime.

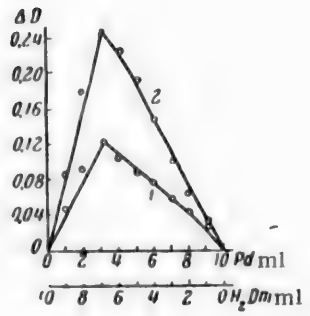


Fig. 2. Deviation of the optical density from additivity on the ΔD – solution composition curve, for a constant excess of trivalent iron. 1) C = $8 \cdot 10^{-5}$ M; 2) C = = $1.6 \cdot 10^{-4}$ M.

The stoichiometric coefficient of trivalent iron in the ternary complex was determined relative to palladium. It was established that when certain conditions are observed, namely, careful addition (dropwise) of the solution of a palladium salt to the solution containing dimethylglyoxime and trivalent iron in a molar ratio of 2 : 1, it is possible to avoid formation of palladium dimethylglyoximate. In this way we succeeded in obtaining a compound with the ratio Pd : H_2Dm : Fe^{III} = 1 : 2 : 1 in solution. Preparation of such a compound at palladium concentrations of the order of 10^{-5} - 10^{-4} g · atom/liter is only possible at pH 3-4,5. Below pH 3 palladium dimethylglyoximate separated out, while at pH > 4.5 ferric hydroxide started to separate out.

The absorption curve of this solution in which $C_{Pd} = 9.5 \times 10^{-5}$ g · atom/liter, $C_{H_2Dm} = 1.9 \times 10^{-4}$ M, and $C_{Fe^{III}} = 9.5 \times 10^{-5}$ g·atom/liter, at pH 3.20, differs slightly from the absorption curve of the solution obtained when trivalent iron is present in excess with respect to palladium (Fig. 1, Curve 2). The absorption maximum is shifted slightly towards the short wavelength side of the spectrum.

The nature of the changes in the optical density of solutions in a series of experiments in which the palladium and dimethylglyoxime concentrations were kept constant at a ratio of 1 : 2, while the concentration of trivalent iron was increased, indicates possible formation of a more complex compound in the system. The optical density of solutions with increasing trivalent iron concentrations increases continuously, and only becomes constant when the iron is present in a considerable excess with respect to palladium (Fig. 4).

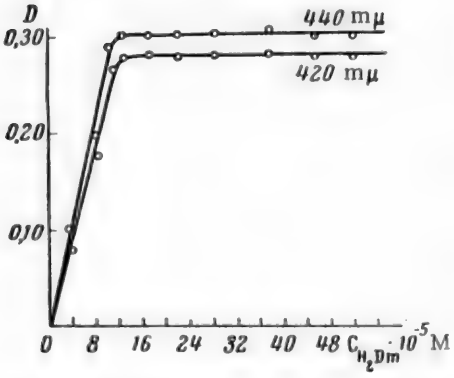


Fig. 3. The relation between the optical density of the solutions and the dimethylglyoxime concentration for constant concentrations of palladium and trivalent iron. $C_{Pd} = 5.8 \cdot 10^{-5}$ M; $C_{Fe^{III}} = 5.8 \cdot 10^{-3}$ M.

In order to determine the stoichiometric coefficient of trivalent iron in the compound formed in the presence of excess iron, we used the "equilibrium shift" method [10]; we modified this method slightly in order to apply it under our experimental conditions*. Bearing in mind the possibility that complexes having different iron contents may be present in solution at the same time, we tried to determine the concentration of each of them under conditions such that

$$D_{solution} = \epsilon_2 X_1 + \epsilon_2 X_2, \quad (1)$$

$$C_{Pd} = X_1 + X_2 + P, \quad (2)$$

where ϵ_1 and ϵ_2 are the molar extinction coefficients of the complexes; X_1 and X_2 are the equilibrium concentrations of the complexes; and P is the palladium concentration in solution, which is determined by the solubility of palladium dimethylglyoximate under the given conditions.

The molar extinction coefficients of the higher complex (ϵ_2) were determined in solutions containing a hundredfold excess of trivalent iron.

* We regarded this second process as a case of stepwise complex formation, i. e., formation of a more complex ternary compound from the simpler compound which has a ratio of Pd : H_2Dm : Fe^{III} = 1 : 2 : 1.

We calculated the molar extinction coefficients of the complex in which the ratio of the components is Pd : H_2Dm : Fe^{III} = 1 : 2 : 1, on the basis of the optical densities of solutions of this compound, taking into account that the equilibrium concentration of the complex in the given instance is equal to the difference $C_{Pd} - P$.

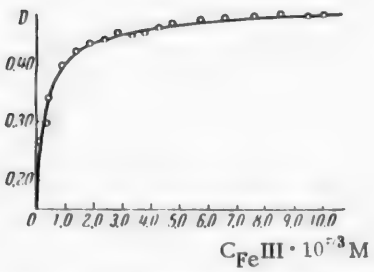


Fig. 4. The relation between the optical density and trivalent iron concentration when the palladium and dimethylglyoxime concentrations are constant. $C_{Pd} = 9.5 \cdot 10^{-5}$ M; $C_{H_2Dm} = 1.9 \cdot 10^{-4}$ M; λ = 440 mμ; l = 10 cm.

According to our results*, at pH 3 and at room temperature, P = 4.3×10^{-8} g·atom/liter, which gives the following mean values for the molar extinction coefficient:

ε_1	ε_2
$\varepsilon_{440} = 2627 \pm 05$	$\varepsilon_{440} = 5161 \pm 45$
$\varepsilon_{470} = 2428 \pm 27$	$\varepsilon_{470} = 4694 \pm 20$
$\varepsilon_{500} = 1926 \pm 30$	$\varepsilon_{500} = 3531 \pm 20$

Having solved equations (1) and (2), and determined the mean values of X_1 and X_2 on the basis of optical density measurements in three parts of the spectrum, we constructed a curve within the coordinates log X_2/X_1, log $[Fe^{III}]$. As shown in Fig. 5, tangent α = 1, this indicates that in increasing the trivalent iron concentration, a further ion of Fe^{III} adds on to the simpler complex in which the ratio of the components is Pd : H_2Dm : Fe^{III} = 1 : 2 : 1 to form a second compound in which Pd : H_2Dm : Fe^{III} = 1 : 2 : 2.

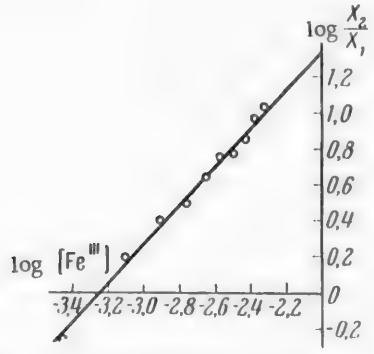


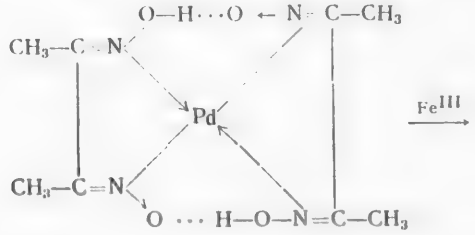
Fig. 5. Determination of the stoichiometric coefficient of iron by the "equilibrium shift" method.

We can only assess the stability of the compound formed approximately. The first stepwise instability constant, determined graphically by the "equilibrium shift" method, was found to be of the order of 10^{-3} (Fig. 5).

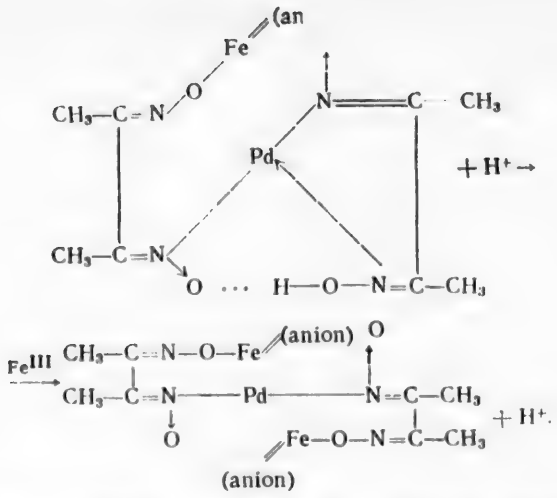
As for the second stepwise instability constant, we can only say that it should be of an order not greater than 10^{-9}, when one bears in mind that the limiting equilibrium concentrations of trivalent iron and palladium in solution are determined by the value of the solubility of palladium dimethylglyoximate at the given hydrogen ion concentration, otherwise, a precipitate of palladium dimethylglyoximate would be formed.

In alkaline solutions obtained on adding either ammonia or the caustic alkalis, no interaction was observed between dimethylglyoxime palladium, and trivalent iron. At a ratio of Pd : H_2Dm : Fe^{III} = 1 : 2 : 1 a precipitate of ferric hydroxide formed; when excess dimethylglyoxime was present, ferric hydroxide was not precipitated because of the formation of ferric dimethylglyoximate [9, 11, 12].

On the basis of the results obtained, the following possible ways in which the ternary compound is formed can be suggested. Presumably, trivalent iron, on reacting with palladium dimethylglyoximate in an acid medium, successively replaces the hydrogen ion of the oxime group according to the following scheme:



* Since the requisite data could not be found in the literature, we determined the solubility of palladium dimethylglyoximate in 0.5, 1.5, and 2 N $HClO_4$ solutions at room temperature, and found the solubility at pH 3 and pH 2 by extrapolation.



It is probable that substitution of hydrogen by trivalent iron is connected with the simultaneous destruction of the coordination bond between palladium and the oxime group. This assumption follows from the fact that palladium dimethylglyoximate dissolves in alkalis.

Excess OH^- ions favors a weakening of the H–O bond in the oxime group; the hydrogen bond is destroyed and makes the substitution of H^+ by an alkali metal possible. The formation of a compound which is readily soluble in water is probably connected with the destruction of the coordination bond in the molecule.*

SUMMARY

It has been shown that palladium, dimethylglyoxime, and iron can interact in aqueous solutions.

Two ternary compounds in which the ratio Pd : H_2Dm : Fe^{III} = 1 : 2 : 1 and 1 : 2 : 2 respectively are formed in weakly acid media.

Ternary compounds are not formed in alkaline media.

The stability of the compounds formed has been assessed approximately, and possible reactions which lead to their formation have been outlined.

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* Feigl assumes [13] that when palladium dimethylglyoximate dissolves in alkalis, an inner complex anion is formed, so that he regards palladium dimethylglyoximate as a compound which functions as an inner complex salt in neutral and acid solutions, and as an acid in alkali solutions.

POLAROGRAPHIC AND AMPEROMETRIC DETERMINATION OF RUTHENIUM

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Most of the published methods for the polarographic determination of ruthenium [1] cannot be included in a general scheme of analysis for the platinum metals. The reason for this is either the impossibility of converting all the ruthenium quantitatively into a compound suitable for polarographic determination [2, 3], the instability of the ruthenium compound chosen for its polarographic determination [4], the impossibility of determining moderate amounts of ruthenium ($10^{-3}-10^{-5}$ M) [5, 6], or the insufficient sensitivity of the method [7].

The polarographic method [8] which we suggested earlier for the determination of ruthenium on the basis of the reduction wave of $K_4Ru_2OCl_{10}$ on a platinum electrode, also has a number of disadvantages. As a result of the slowness and irreversibility of the electrode reaction for the reduction of $[Ru_2OCl_{10}]^{4-}$ on a rotating electrode, extended curves without a clear cut diffusion current region are obtained, which cannot be recommended for the quantitative determination of ruthenium. The use of a stationary electrode also has its drawbacks, and, in addition, does not permit determination of less than 5 μg Ru/ml. Platinum, palladium, iridium, gold, and dissolved oxygen should interfere with polarographic determination of ruthenium. More recently [9] we have found a simple method of preparing solutions of sodium hexachlororuthenate (Na_2RuCl_6), which is reversibly reduced on a platinum electrode, and which gives clearly defined waves with $E_{1/2}$ equal to 0.72 v (with respect to the saturated calomel electrode) (Fig. 1) on both stationary and rotating platinum electrodes. Experiments have shown that solutions of sodium hexachlororuthenate in 6 N hydrochloric acid are fairly stable. The polarographic wave of $[RuCl_6]^{2-}$ corresponds to its reduction to $[Ru(H_2O)Cl_5]^{2-}$. As a result, the platinum electrode is not contaminated by metal which might separate out during reduction, and there is no need for special cleaning operations, which appreciably simplifies its use. All these advantages led us to use hexachlororuthenate for the polarographic determination of ruthenium.

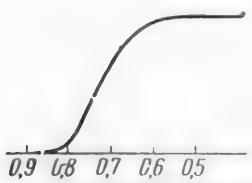

Fig. 1. Polarographic curve for Na_2RuCl_6.

$[RuCl_6]^{2-}$ ions are reduced on a platinum electrode in the same potential range as $[IrCl_6]^{2-}$ ions. Accordingly, we tried to titrate ruthenium amperometrically with the same reducing agent which we used earlier for the titration of iridium, namely, hydroquinone [10]. Apart from hydroquinone, ascorbic acid can also be used for titrating ruthenium. Since, however, standard solutions of ascorbic acid do not keep well (their factors change with time), ascorbic acid is less suitable.

Apparatus and Reagents. Polarograms were taken on the LP 55 instrument (a Czech instrument) with a galvanometer whose sensitivity was 3.52×10^{-3} μa/mm for anodic-cathodic polarization. The galvanometer readings were read off visually on an extension scale 40 cm long with the zero at the middle. The voltage was altered manually. The cathode was a rotating platinum electrode 5 mm long, 0.5 mm in diameter. This elec-

trode was rotated at the rate of about 800 rpm. A saturated calomel electrode with a large mercury surface (35 mm in diameter) was used as the anode. The volume of the electrolytic cell was 20 ml. Amperometric titration was carried out in the same apparatus as that used for taking polarograms. The titrant solution was added from a microburet with scale divisions of 0.02 ml. A standard ruthenium solution (T = 0.03 and 0.103 mg/ml) was prepared from the distillate obtained on distilling RuO_4; the RuO_4 was distilled from a sulfuric acid solution by means of sodium bromate, and absorbed in hydrochloric acid. The distillate was evaporated almost to dryness, it was then boiled with 2 N hydrochloric acid and diluted with 2 N HCl to the requisite volume. The solution was standardized gravimetrically by means of thionalide.

The hydroquinone solutions used as the titrant were prepared by dissolving accurately weighed aliquots of the commercial reagent. In order to increase the stability of these solutions, they were prepared in twice distilled water, and 10 ml hydrochloric acid added per liter. The solutions were standardized by amperometric titration with the Na_2IrCl_6 solution. Periodic checks on the factor of the solutions, showed that solutions of hydroquinone prepared as described, are stable for more than two months. Simon and Zyka [11], in some work which they carried out specially for this purpose, also demonstrated the high stability of hydroquinone solutions. Hydroquinone solutions, 1 ml of which corresponded to 0.1, 1.0, and 5.0 mg of ruthenium respectively were used as titrants.

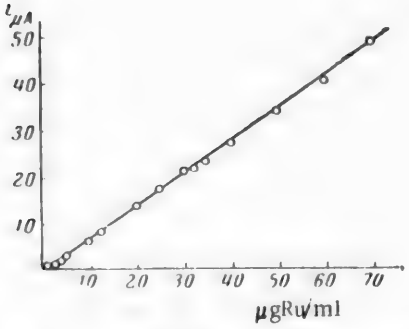

Fig. 2. The relation between the diffusion current and ruthenium concentration.

Polarographic Determination of Ruthenium. The technique used for preparing the Na_2RuCl_6 solutions in order to take polarograms was as follows:

The solution containing a mixture of the various complex chlorides of ruthenium was evaporated to dryness on a water bath, after having added a small amount of sodium chloride. Five ml of 0.8-1.0 N HCl and 5-6 drops of hydrogen peroxide were then added, and the solution heated until the solution was colorless or had a slight rosy-yellow color (for ruthenium contents greater than 80 μg/ml). $Na_2Ru(H_2O)Cl_5$ is thereby formed. An equal volume of concentrated hydrochloric acid was added and heating continued on a water bath until only a moderate amount of bubbles came off. The solution of Na_2RuCl_6 was boiled on a hot plate for 5 min to remove chlorine, it was rapidly cooled, diluted with hydrochloric acid (1 : 1) to 10 ml, and polarograms taken over the range +0.9 to +0.5 v.

The polarograms obtained for solutions with various ruthenium contents, prepared by the method described, showed that the diffusion current of quadrivalent ruthenium is proportional to its concentration from 1×10^{-5} to 2×10^{-3} M (from 1 to 200 μg/ml) (Fig. 2). This proportionality is observed with an accuracy of up to 1.5%. The reproducibility of the diffusion currents obtained when taking polarograms of parallel samples was about 2.5% for samples containing 1-10 μg Ru/ml, while for higher Ru concentrations, the reproducibility was 0.5 %. The minimum amount of ruthenium which can be determined is 1 μg/ml. The accuracy of the method is not high enough for taking polarograms of solutions containing more than 200 μg Ru/ml. The error in these cases may arise during preparation of the solutions, since at high Ru concentrations it is difficult to decide on the completeness of the conversion into $Na_2Ru(H_2O)Cl_5$ from the change in the color of the solution, during the interaction of the original solution with hydrogen peroxide. Accordingly, during determination of large amounts of ruthenium, it is best to taken an aliquot of the solution. Chlorine is formed during the preparation of $[RuCl_6]^{2-}$ by the interaction of 6 N HCl with hydrogen peroxide. In the presence of chlorine, the first part of the polarogram of quadrivalent ruthenium is strongly distorted; chlorine must therefore be removed from the solution. A stream of carbon dioxide can be used for this purpose. Such a method, however, takes a long time—up to 40 min. We therefore removed chlorine by boiling the solution. Since gradual reduction of Ru^{IV} occurs on heating Na_2RuCl_6 solutions, the time for which solutions are boiled should not exceed 5 min for solutions containing hundredths of a milligram in 10 ml. More concentrated solutions can be boiled for 10-12 min.

Measurements of the wave height for Na_2RuCl_6 solutions carried out at different temperatures, showed that the diffusion current of quadrivalent ruthenium increases by approximately 2% per degree. Nevertheless, since on prolonged heating partial reduction of $[RuCl_6]^{2-}$ occurs, the actual increase of the diffusion current with

TABLE 1

Amperometric Titration of Na_2RuCl_6 with Hydroquinone

Ru, mg		Absolute error, mg	Relative error, %	Ru, mg		Absolute error, mg	Relative error, %	Ru, mg		Absolute error, mg	Relative error, %
taken	found			taken	found			taken	found		
0,95	0,92	—0,03	—3,1	0,20	0,21	+0,01	+5,0	0,040	0,039	—0,001	— 2,5
0,80	0,82	+0,02	+2,5	0,10	0,10	0	0	0,020	0,021	+0,001	+ 5,0
0,70	0,68	—0,02	—2,8	0,090	0,090	0	0	0,010	0,009	—0,001	—10,0
0,50	0,50	0	0	0,070	0,071	+0,001	+1,4	2,00	1,91	—0,09	— 4,7
0,40	0,40	0	0	0,060	0,059	—0,001	—1,7	4,00	4,24	+0,24	+ 3,0
0,30	0,29	—0,01	—3,3	0,050	0,049	—0,001	—2,0	6,00	5,62	—0,38	— 6,3

TABLE 2

Determination of Ruthenium in Industrial Products

Material	Ru determined, %			
	gravimetrically	photometrically	potentiometrically	amperometrically
№ 1	0,027	—	—	0,026
№ 2	0,048	0,042	—	0,046
№ 3	—	0,21	—	0,19
№ 4	2,16	—	2,11	2,12

temperature is considerably higher. Having determined $[RuCl_6]^{2-}$ in solution, after heating the solutions to 40-50°, we calculated that the temperature coefficient of the diffusion current of $[RuCl_6]^{2-}$ as equal to 3.3% per degree. This significant change in current with temperature must be borne in mind during the polarographic determination of ruthenium. In order to avoid temperature effects, immediately after taking polarograms of a test solution, we took polarograms of a standard solution prepared at the same time. The amount of ruthenium was determined by comparison with the standard solution. Another method which can be recommended is thermostatting of the electrolytic cell, and determination of the ruthenium from a calibration curve obtained at a definite temperature.

When solutions of Na_2RuCl_6 are allowed to stand for a long time, gradual reduction to $Na_2Ru(H_2O)Cl_6$ occurs. Test solutions should not therefore be kept for a long time. Experiments have shown that polarograms of dilute solutions (1-10 μg Ru/ml) should be taken not later than 45 min after their preparation. More concentrated solutions can be kept without any changes for several hours.

Large amounts of rhodium, platinum, palladium, and osmium do not interfere with the polarographic determination of ruthenium, since the complex chlorides of these elements are reduced at appreciably more negative potentials. Iridium interferes, since the half-wave potential of $[IrCl_6]^{2-}$ is about 0.7 v. $[AuCl_4]^-$ starts to be reduced at +0.5 v, and therefore gold does not interfere in small amounts. On increasing the gold concentration, the area of the limiting current of ruthenium decreases, and when the amount of gold present is 15 times that of the ruthenium, determination of the latter becomes very difficult. Copper, nickel, selenium, and tellurium do not affect the ruthenium polarographic wave. Trivalent iron starts to be reduced at +0.5 v, and when the iron present is ten times the ruthenium, the iron wave fuses with the ruthenium wave. Large amounts of iron also complicate ruthenium determination because of the formation, during preparation of the solution, of ferrous ions which reduce the quadrivalent ruthenium. In order to oxidize all the ferrous iron it is necessary to add a large amount of hydrogen peroxide and carry out the oxidation in a more acid medium, otherwise the ruthenium results are low. Atmospheric oxygen does not interfere so that open electrolytic cells can be used. It was par-

ticularly important to establish the effect of sulfur dioxide, since in many of the analytical schemes adopted for the analysis of ruthenium, the latter is separated from all remaining elements in the form of its tetroxide which is absorbed by hydrochloric acid saturated with sulfur dioxide. When a distillate obtained in this way is evaporated to dryness and then subjected to all the operations described above for converting the ruthenium into Na_2RuCl_6, low results are always obtained for ruthenium. The reason for this is that probably some of the ruthenium forms complex sulfite- or sulfate compounds, which, even in dilute hydrochloric acid solutions are oxidized by hydrogen peroxide to the volatile tetroxides. It is therefore essential to destroy these compounds carefully by repeated evaporation of the solution with concentrated hydrochloric acid in the presence of sodium chloride.

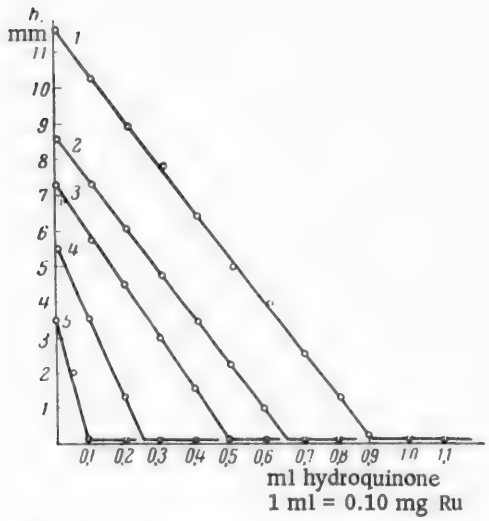

Fig. 3. Curves obtained during the amperometric titration of ruthenium with hydroquinone. 1) 0.90 mg Ru; 2) 0.70 mg Ru; 3) 0.50 mg Ru; 4) 0.25 mg Ru; 5) 0.10 mg Ru.

Conversion of all the ruthenium into Na_2RuCl_6 is much easier when, during the distillation of RuO_4, hydrochloric acid saturated with sulfur dioxide is used only in the last receivers. The contents of the last receivers which only contain a small amount of the ruthenium must be evaporated several times with hydrochloric acid, and only after this stage, combined with the contents of the first receivers which do not contain any sulfur dioxide.

Amperometric Titration of Ruthenium with Hydroquinone Solution. Preliminary experiments showed that hydroquinone very rapidly reduces $[RuCl_6]^{2-}$ at room temperature [9]. Reduction proceeds stoichiometrically according to the equation

$$2Na_2RuCl_6 + C_6H_4(OH)_2 + H_2O = 2Na_2Ru(H_2O)Cl_5 + C_6H_4O_2 + 2HCl$$

Amperometric titration was carried out on the basis of the cathode current of quadrivalent ruthenium at a potential of +0.5 v (relative to the saturated calomel electrode). At this potential the hydroquinone does not give a reduction wave, and the titration curves are of the shape shown in Fig. 3. The break at the end point is very clear. Preparation of solutions for amperometric titration reduces to preparing solutions of Na_2RuCl_6, and is exactly the same as the preparation of the solutions used for taking polarograms. As titration proceeds the color of the solution lightens, and at the end point, depending on the ruthenium concentration, the solution becomes colorless, or acquires a slight rosy shade. The method can be used for 0.02-2.0 mg of ruthenium (Table 1).

The relative error for the determination of tenths and hundredths of a milligram is 1-5%. The mean reproducibility of the results, including preparation of the solutions, is 2.5%. Titration of more than 2 mg of ruthenium is complicated for the same reason as that outlined for polarographic determination of ruthenium.

Platinum, palladium, rhodium, osmium, copper, nickel, selenium, and tellurium do not interfere with the amperometric titration of ruthenium. When gold is present, the current at the end point is greater than zero; nevertheless, the break on the titration curve at the end point is still quite distinct when the amount of gold present is 20 times that of ruthenium. $[AuCl_4]^-$ ions are only slowly reduced at room temperature by hydroquinone, so that ruthenium can be determined in the presence of 15-20 times its amount of gold. Trivalent iron does not interfere with the titration as long as the amount of it present is not more than 5-10 times that of ruthenium. All the divalent iron must, however, be oxidized. Iridium interferes.

Sulfur dioxide and chlorine interfere with the amperometric titration of ruthenium for the same reasons as they interfere with its polarographic determination; the methods used for eliminating such interference are the same as those described above.

Amperometric titration of ruthenium has some advantages over its polarographic determination; the experimental conditions do not have to be observed so rigidly (temperature, rotational rate of the electrode, and the

parameters of the latter), and there is no need to prepare a standard solution at the same time as the test solution, or to construct a calibration curve.

We have used the amperometric method for the determination of ruthenium in some industrial products. The results obtained are in satisfactory agreement with those obtained by gravimetric, photometric, and potentiometric methods (Table 2).

SUMMARY

A method has been developed for the polarographic determination of ruthenium on the basis of the reduction wave of $[RuCl_6]^{2-}$ on a platinum electrode. The method can be used for the determination of 1 to 200 μg Ru/ml in the presence of platinum, palladium, rhodium, osmium, and some base metals.

A method has been developed for the amperometric titration of Na_2RuCl_6 with hydroquinone solutions, using a rotating platinum electrode. The method is suitable for the determination of the same amounts of ruthenium determined by the polarographic method, but it is simpler to carry out than the polarographic method.

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DETERMINATION OF WATER IN COMPOUNDS BY THE HYDRIDE METHOD

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The hydride method suggested by Elitsur [1], in which pyridine is used as the medium, is often used for the determination of water in aquocomplex compounds. Essentially, the method depends on the fact that the pyridine, which is in contact with the test compound, removes the water from it and forms a thermally stable hydrate $C_5H_5N \times H_2O$; the latter is then decomposed with calcium hydride with the liberation of a definite amount of hydrogen ($CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$). The method has been checked on various compounds and only a few exceptions have been found in which incorrect results were obtained. These exceptions include very stable crystallohydrates (e. g., $BeSO_4 \cdot 4H_2O$) which do not give up their water completely under the experimental conditions used (water bath temperature), and also compounds which are readily reduced with liberation of gaseous products. Thus, only one reason has been advanced for explaining cases were high results have been obtained—reduction of the test compounds in contact with pyridine and calcium hydride.

According to the technique suggested by Elitsur, the pyridine is finally dehydrated prior to its use by heating a mixture of pyridine and calcium hydride in the reaction vessel on a water bath; after cooling, an aliquot of the test material is then introduced into the vessel. As the result of the interaction of water with calcium hydride, both during preliminary dehydration of pyridine and during the actual determination, a large amount of calcium hydroxide is formed, and this is a strong base whose effect on the test preparations cannot be ignored.

In order to define more closely the limits of the applicability of the hydride method of determining water, we have studied the interaction of mixtures of pyridine and calcium hydride (and calcium hydroxide) with the compounds of the elements of some of the groups in the Periodic System, in particular, with elements which possess amphoteric properties.

EXPERIMENTAL

The simple and complex chlorides of the elements were chosen mainly for our studies.

The anhydrous chlorides of aluminum, iron, zirconium, and tantalum were prepared by chlorination of the corresponding metals with gaseous chlorine; they were stored in sealed vessels in a desiccator over phosphorus pentoxide. Ammonium sulfate and chloride, chemically pure grade, were given a preliminary drying at 200-250°, while zirconium chloride hexahydrate was obtained by keeping the chemically pure octahydrate in a desiccator over sulfuric acid sp. gr. 1.84, until it had reached constant weight. The preparation of the hexachlorotitanates and chlorooxytitanates of the aklai metals and ammonia, as well as the preparation of titanium trichloride hexahydrate have been described previously [2, 3].

Pyridine was completely dehydrated as follows. Technical pyridine was distilled over calcium hydride; subsequently, the pyridine was kept in contact with calcium hydride for several months, and then redistilled over calcium hydride. The calcium hydride, pure grade, (containing calcium hydroxide as impurity) used for de-

Compound	Aliquot, g	No. of moles H_2 per mole of compound	Water content, % wt.	
			theoretical content	calc. on basis of H_2 liberated
NH_4Cl	0,0811	0,5	0	16,78
$(NH_4)_2SO_4$	0,2122	1	0	13,74
$AlCl_3$	0,0329	1	0	13,35
Cs_2TiCl_6	0,1340	2	0	6,86
$(NH_4)_2TiCl_6$	0,0951	3	0	18,39
$Cs_2TiOCl_4 \cdot H_2O$	0,1225	2	3,68	7,33
$Rb_2TiOCl_4 \cdot H_2O$	0,1155	2	4,56	9,07
$3NH_4Cl \cdot 2TiOCl_2 \cdot 4H_2O$	0,1400	7,5	14,35	27,92
$ZrCl_4$	0,1294	1,25	0	9,62
$ZrOCl_2 \cdot 6H_2O$	0,3760	5,66	37,74	35,6
$TiO_2 \cdot nH_2O$	0,5309	0,26	13,10*	5,11
$TiCl_3 \cdot 6H_2O$	0,0597	6	41,19	41,07
$TaCl_5$	0,2503	2	0	9,75
$FeCl_3$	0,1536	1	0	11,93

* Water was determined by loss in weight on calcining.

composing traces of calcium nitride with the traces of moisture in the pyridine, was heated with pyridine on a water bath in the apparatus which was subsequently used for water determination. No calcium hydroxide was added, since we observed that it always appeared in the reaction mixture during preliminary dehydration of pyridine.

The technique used has been described in detail in Elitsur's article [1].

As the results in the table show, of all the compounds tested, only titanium trichloride hexahydrate contained the amount of water, calculated on the basis of the amount of hydrogen liberated, which was equal to the theoretical value. A certain amount of hydrogen was liberated even during the interaction of the anhydrous chlorides of titanium, zirconium, tantalum, iron, aluminum, and ammonia with a mixture of pyridine, calcium hydride, and calcium hydroxide.

The explanation for this lies in the fact that all the compounds listed interact with the calcium hydroxide in the reaction mixture, as a result of which the hydroxides of the respective metals are formed. Formation of hydroxides were observed in some cases experimentally; amorphous flocculent precipitates appeared in the mixture, and sometimes these floated to the surface. This process was very rapid in those cases where the chloride dissolved in pyridine (e. g. $TiCl_3$, $ZrCl_4$) and optimum conditions were obtained for contact with the calcium hydroxide. In the case of insoluble compounds (e. g. NH_4Cl, $(NH_4)_2SO_4$), the reaction process was speeded up by stirring the reaction mixture. Of course, compounds of group I and II elements do not react with calcium hydroxide and do not give high water contents during their determination.

The hydroxides formed are distinguished by differences in the stability of the water bond; this stability can be characterized by the temperature at which the water is split off on heating. Ammonium hydroxide is an unstable compound and immediately it is formed it gives up water to the pyridine; the hydrate of the latter interacts with calcium hydride to liberate hydrogen at the rate of 0.5 mole per 1 g · ion of ammonia, and this was actually observed in practice:

$$4NH_4Cl + 2Ca(OH)_2 = 2CaCl_2 + 4NH_3 + 2H_2O$$
$$2H_2O + CaH_2 = Ca(OH)_2 + 2H_2$$
$$\overline{4NH_4Cl + Ca(OH)_2 + CaH_2 = 2CaCl_2 + 4NH_3 + 2H_2}$$

The hydroxides of the elements tested can be divided into two groups: the elements of one group give up all their water under reaction conditions and give oxides, apparently, as the final product; the elements of the other group give up only a part of their water.

According to our results, one mole of the anhydrous chlorides of aluminum and iron liberated one mole of hydrogen during the reaction; the reactions which occur can be expressed by the following equations:

$$2Me^{III}Cl_3+3Ca(OH)_2=3CaCl_2+2Me^{III}(OH)_3$$
$$2Me^{III}(OH)_3+2CaH_2=2Ca(OH)_2+2Me^{III}O(OH)+2H_2$$
$$2Me^{III}Cl_3+Ca(OH)_2+2CaH_2=3CaCl_2+2Me^{III}O(OH)+2H_2$$

These results agree with published data* on aluminum hydroxide. During the interaction of aluminum salts with alkali, the ortho hydrated oxide $Al(OH)_3$ is formed, which splits off part of the water and is converted into the considerably more stable meta-form of the hydroxide AlO(OH). AlO(OH) is formed at temperatures below 170°.

By analogy, tantalum hydroxide presumably splits off two molecules of water, since two moles of hydrogen are formed per mole of $TaCl_5$ during the reaction.

In the case of zirconium compounds, the number of moles of H_2 split off per mole of the compounds is a fraction. Forms with a definite composition are not known for zirconium hydroxides. Dehydration of the hydroxides starts at a low temperature and proceeds gradually with increasing temperature. Some water, 0.75 mole per mole of ZrO_2, remains in the hydroxide at a temperature of about 120° [4].

During determination of water in quadrivalent titanium compounds, we established that one mole of $TiCl_4$ splits off an additional two moles of hydrogen, while one mole of $TiOCl_2$ splits off one mole of H_2. According to these results, the reactions proceed as follows:

$$TiCl_4+2Ca(OH)_2=Ti(OH)_4+2CaCl_2$$
$$Ti(OH)_4+CaH_2=TiO_2+Ca(OH)_2+2H_2$$
$$TiCl_4+Ca(OH)_2+CaH_2=TiO_2+2CaCl_2+2H_2,$$

$$2TiOCl_2+2Ca(OH)_2=2TiO(OH)_2+2CaCl_2$$
$$2TiO(OH)_2+CaH_2=2TiO_2+Ca(OH)_2+2H_2$$
$$2TiOCl_2+Ca(OH)_2+CaH_2=2TiO_2+2CaCl_2+2H_2$$

Nevertheless, thermal analysis which we carried out on titanium hydroxides, precipitated both hydrolytically from solution, and by ammonia, showed that a large fraction of the water is split off at 120°, but not all the water. All the water in the hydroxide is not determined by Elitsur's method either. It is possible that this deviation can be explained by the fact that pyridine reacts with titanium hydroxide at the moment it is formed, and its properties may differ from those of the gell of titanic acid dried over a long period.

Trivalent titanium hydroxide, under conditions which exclude oxidation, is a stable compound, and, presumably, holds the water of constitution more firmly than does pyridine; accordingly liberation of six moles of hydrogen per mole of titanium trichloride hexahydrate is observed, in agreement with the known water content.

On the basis of our results and those of Elitsur, the following conclusions can be drawn.

When a simple or complex compound does not decompose in a pyridine medium, then the amount of constitutional water will be determined by the hydride–pyridine method, as long as the temperature at which the compound splits off water does not exceed about 170°. It should be noted that many compounds, e. g., $TiCl_3 \cdot 6H_2O$, and the chlorooxytitanates of the alkali metals, are decomposed by pyridine, and thereby liberate water which reacts with the calcium hydride.

When the compound of any element interacts with the calcium hydroxide present in the reaction mixture, then correct determination of water in the compound depends on the bond stability of the constitutional water in the hydroxide of this element; the water which is split off from the hydroxide at temperatures below 150-170° will react with calcium hydride. Most of the compounds of many of the elements in III, IV, V and the subsequent groups of the Periodic System will, presumably, belong to this group.

*The data on the hydroxides were taken from "Gmelins Handbuch der Anorganischen Chemie"; no reference to the source was given in the handbook.

SUMMARY

The range over which the hydride method with pyridine can be used is very limited. Compounds of aluminum, iron, lanthanum, and cerium which, according to the results given in Elitsur's article, give correct values for their water content, should give high values for water, since the hydroxides of lanthanum, cerium, and other rare earth elements split off part of their water at temperatures below 150° [5].

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ANALYSIS OF THE BORIDES OF THE TRANSITIONAL AND RARE EARTH ELEMENTS

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Amorphous boron can be oxidized to boric acid by potassium permanganate [1], ceric sulfate [2], a mixture of hydrogen peroxide and nitric acid [3], and also by potassium iodate and periodate [4]. A method which has been developed for the determination of free boron in boron carbide [5] is based on the difference in the oxidizability of free boron and of boron combined as the carbide.

In the work described here we studied the behavior of the borides of the transitional elements: TiB_2, ZrB_2, CrB_2, W_2B_5 and the hexaborides of the rare earths: Y, La, Ce, Pr, Nd, Sm, Gd towards various oxidizing mixtures capable of oxidizing amorphous boron: a nitric acid – hydrogen peroxide mixture, a sulfuric acid solution of potassium iodate, and a sulfuric acid solution of ceric sulfate. It was thought that it might be possible, on the basis of differences in the stability of free boron and of the borides listed above to the oxidizing mixtures mentioned, to develop a technique for determining free boron in these borides.

The Stability of the Borides in Solutions of Hydrogen Peroxide and Nitric Acid. An aliquot of the finely ground boride (270 mesh) was treated with the reagent in a flask made of boron-free glass, and fitted with a ground glass reflux condenser. When the aliquot was not decomposed completely, the insoluble residue was filtered off on a glass filter, thoroughly washed with water, dried to constant weight, and weighed. An aliquot of this dried residue was taken for repeated treatment with the oxidizing mixture. The boron and metal contents of the filtrate were determined.

Borides with the chemical composition given in Table 1 were used in the work.

During a study of the stability of the borides in solutions consisting of mixtures of hydrogen peroxide and nitric acid, it was observed that zirconium diboride was the most stable compound toward this oxidizing mixture. The remainder of the borides listed above were either decomposed completely by the mixture (YB_6, LaB_6, CeB_6, PrB_6, NdB_6, SmB_6, GdB_6), or partially (CrB_2, TiB_2, W_2B_5) decomposed within the time indicated.

In view of these findings, only the oxidation of ZrB_2 by the hydrogen peroxide–nitric acid mixture was studied in detail.

As the results in Table 2 show, the same amount of boron dissolved, independently of the time for which the boride was treated, and of the hydrogen peroxide concentration.

The residue obtained after the first treatment with the hydrogen peroxide–nitric acid mixture was treated a second time with the same mixture over a similar time period. It was established that during the second treatment of zirconium boride with the oxidizing mixture no boron dissolved. These results indicate that it should be possible to determine free boron in zirconium boride.

In order to check on the method suggested, a series of determinations of free boron in synthetic mixtures of ZrB_2 and amorphous boron was carried out. The results obtained are given in Table 3.

TABLE 1

Chemical Composition of the Borides

Transitional metal borides				Rare earth hexaborides			
boride	content, %			boride	content, %		
	metal	B	C_{formed}		metal	B	C_{formed}
ZrB_2	82,0	18,0	—	YB_6	59,4	40,6	—
	82,9	16,0	—				
CrB_2	69,7	28,9	0,4	LaB_6	69,35	30,60	—
TiB_2	69,05	30,0	0,35	CeB_6	68,8	27,7	0,13
W_2B_5	88,0	11,30	0,3	PrB_6	70,1	30,1	—
				NdB_6	70,9	27,65	—
				SmB_6	71,20	27,5	0,2
				GdB_6	71,9	28,2	—

TABLE 2

Primary Treatment of ZrB_2 with Hydrogen Peroxide–Nitric Acid

Sample No.	Mixture of 20 ml hydrogen peroxide (1 : 3) and 10 drops HNO_3					Mixture of 20 ml hydrogen peroxide (1 : 2) and 10 drops HNO_3				
	sample wt g	time of treatment	0.1 N NaOH ml	0.1 N NaOH in the blank, ml	% Boron (free)	sample wt., g	time of treatment	0.1 N NaOH ml	0.1 N NaOH in the blank, ml	% Boron (free)
I	1,0	30	1,15	0,3	0,090	1,0	30	1,20	0,4	0,085
	1,0	45	1,20	0,3	0,097	1,0	45	1,20	0,4	0,085
	1,0	60	1,10	0,25	0,085	1,0	60	1,25	0,4	0,090
	0,5	30	0,70	0,3	0,085					
	0,5	45	0,70	0,25	0,090					
II	1,0	30	0,30	0,25	Free boron	1,0	30	0,35	0,40	Free boron
	1,0	45	0,30	0,30	absent	1,0	45	0,35	0,35	absent
	1,0	60	0,30	0,25		1,0	60	0,40	0,40	
	0,5	30	0,30	0,30						

TABLE 3

Determination of Free Boron in Synthetic Mixtures Containing Amorphous Boron (Weight of ZrB_2 taken was 0.5 g. Dissolution was carried out in hydrogen peroxide (1 : 3) and 10 drops of HNO_3)

Boron added, mg	8,30	14,90	20,60	23,10	30,30	43,00	49,0	51,0
Boron found, mg	8,48	14,97	20,29	22,81	29,87	42,46	48,90	50,75
Relative error, %	+2,16	+0,47	—1,5	—1,25	—1,41	—1,25	—0,2	—0,5

It is clear from these results that the free boron content of zirconium boride can be determined with reasonable accuracy by the method suggested.

Analytical Procedure. A 1-g aliquot of zirconium boride is dissolved on heating for 30-40 min in 20 ml of hydrogen peroxide (1 : 3) and ten drops of nitric acid, contained in a flask fitted with a reflux condenser. The residue is filtered off. The filtrate is neutralized, first by 10% NaOH solution free from carbonate, and then with

TABLE 4

The Solubility of the Borides of the Rare Earths and Thorium in Acids and Mixtures of Acids

Boride	HNO_3 (1:1)	Aqua regia (1:1)	H_2SO_4 1:1 +5 drops of HNO_3	HCl (1:1)	H_2SO_4 (1:1)
YB_6	Complete dissolution on gentle heating for 5 min.	Complete dissolution in the cold or on gentle heating for 5 min.	Complete dissolution on gentle heating for 5 min.	77—78%	71—72%
LaB_6				93—94%	89—92%
CeB_6				84—86%	83—84%
PrB_6				90—94%	27—30%
NdB_6				87—88%	78%
SmB_6				79—80%	77%
GdB_6				91—93%	87%
ThB_6				82%	

0.1 N or 0.01 N NaOH to the methyl red end point. Ten ml of a neutral solution of inert sugar or 1 g of mannitol is added, and the boric acid titrated to the phenolphthalein end point with 0.1 N or 0.01 N sodium hydroxide.

Stability of the Borides in Acid Solutions of Potassium Iodate and Ceric Sulfate. The diborides of chromium, titanium, and zirconium, as well as boron nitride and carbide, do not dissolve either in the cold, or on heating, in acid solutions of potassium iodate and periodate [4]. Elemental boron readily dissolves in these solutions, and use has been made of this fact for the determination of boron in elemental boron and in borides (MgB_2, MgB_6, MgB_{12}, CaB_6, BaB_6) [4].

We wanted to use sulfuric acid solutions of potassium iodate and periodate for determining free boron in chromium, titanium, and zirconium diborides and in rare earth elements hexaborides. The experiments which we carried out showed that the borides TiB_2, ZrB_2, CrB_2 and the hexaborides of Y, La, Ce, Nd, Sm, Gd react with a sulfuric acid solution of potassium to liberate iodine. The borides which we tested also proved unstable in acid solutions of ceric sulfate. Consequently, acid solutions of ceric sulfate and potassium iodate could not be used for the determination of free boron in borides.

Acid Stability, Alkali Stability, and Analytical Methods for the Hexaborides of the Rare Earths. The dissolution of the hexaborides of Y, La, Ce, Pr, Nd, Sm, Gd in hydrochloric, nitric, and sulfuric acids and in mixtures of these acids was studied, as well as their dissolution in aqueous alkali solutions. Platinum vessels were used for dissolution of the hexaborides in alkalis.

Results obtained on the solubility of the hexaborides in acids are given in Table 4.

The amount of insoluble residue (%) remaining after treating the borides with acids for two hours is given in the last two columns of this table.

It follows from these results that the rare earth hexaborides listed above are comparatively readily decomposed by acids. In order of their stability in hydrochloric acid, they can be arranged in the following series: LaB_6, PrB_6, GdB_6, NdB_6, CeB_6, SmB_6, YB_6; while in sulfuric acid this order is LaB_6, GdB_6, CeB_6, NdB_6, SmB_6, YB_6, PrB_6.

The rare earth hexaborides hardly dissolve at all in aqueous alkali solutions. The exception is CeB_6 which is decomposed by a mixture of sodium hydroxide and hydrogen peroxide.

Analytical Procedure for the Rare Earth Hexaborides. The hexaboride (0.5 g)(Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Yb, Th) is dissolved on gentle heating in 20 ml of nitric acid (1 : 1) contained in a flask fitted with a reflux condenser. The solution obtained is transferred to a 250 ml standard flask and its volume made up to the mark with water. The rare earth and thorium content is determined by titration with sodium ethylenediaminetetracetate (EDTA-Na) using arsenazo as indicator [6], or gravimetrically by the oxalate method. An aliquot (50 ml) of the solution is transferred to a 350 ml conical flask, 3-5 drops of pyridine is added, and ammonia added to adjust the pH to 6-7, using universal indicator paper; 2-3 drops of a 0.5% aqueous solution of arsenazo

is added and the rare earths titrated with 0.025 M EDTA-Na until the color of the solution changes from violet to yellow-rose. Thorium is titrated at pH 2-4. The EDTA-Na solution is standardized against lanthanum nitrate solution of known concentration.

Boron Determination. For determination of boron in the rare earth borides (with the exception of SmB_6) a method is suggested which does not involve preliminary removal of the rare earth element. The rare earth element is complexed by addition of EDTA-Na, and boron determined by the usual titrimetric method. The exact amount of EDTA-Na must be added to complex the rare earth element. This amount has already been determined during titration of the rare earth element. An aliquot (50 ml) of the solution is transferred to a 300 ml conical flask, and the exact amount of 0.025 M EDTA-Na solution added from a buret. The solution obtained is neutralized with sodium hydroxide using methyl red as the indicator, and boron then determined as usual by titrating it with 0.1 N NaOH using phenolphthalein as the indicator in the presence of mannitol or invert sugar.

The method suggested has been checked by comparing it with the normal method of determining boron, in which the rare earths are removed by precipitation with $BaCO_3$. Satisfactory results were obtained. For determination of boron in the borides of Sm and Th, Sm and Th must be removed by precipitating them with barium carbonate.

SUMMARY

A technique has been developed for the determination of free boron in zirconium boride; it is based on the difference between the oxidizability of free boron and of combined boron with a mixture of hydrogen peroxide and nitric acid.

It has been shown that acid solutions of ceric sulfate and potassium iodate cannot be used for the determination of boron in the borides of Ti, Zr, Cr, W, and the rare earth elements, since the borides themselves are soluble to a considerable extent in these mixtures.

A simple method is suggested for the analysis of the rare earth hexaborides.

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QUANTITATIVE DETERMINATION OF TRACES OF BARIUM, NICKEL, COPPER, ANTIMONY, MOLYBDENUM, MANGANESE, CADMIUM, TIN, GOLD, AND ARSENIC IN METALLIC BERYLLIUM BY A RADIOACTIVATION METHOD

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A radioactivation method has been used for the determination of lithium, nitrogen, fluorine, aluminum, and vanadium present as impurities in metallic beryllium [1]. Work has also been published on the determination of total rare earths [2] and oxygen [3, 5] in beryllium. In the work described here the content of Ba, Ni, Cu, Sb, Mo, Mn, Cd, Sn, Au, As present as impurities in metallic beryllium has been determined on the basis of the activity of the products formed as the result of the capture of thermal neutrons (Ba^{139}, Ni^{65}, Cu^{64}, Mn^{56}, Sb^{122}, Mo^{99}, Cd^{115}, Sn^{121}, Au^{198}, As^{76}).

The basic characteristics of the isotopes used are given in Table 1.

The sensitivity of the determination is calculated for a stream of 0.5×10^{12} neutrons/cm^2, and irradiation time of three hours for 40 decays/sec towards the end of irradiation. The actual sensitivity of the determination is always below the calculated value, since during the time elapsing between the end of irradiation and the beginning of activity measurements, the activity of the element decreases with its half-life period. In addition, not all the activity obtained toward the end of irradiation is measured, because of the loss which occurs during chemical separation and purification.

A relative method was used for determining the content of impurities. The test beryllium samples (1 g) were placed in polyethylene cassettes, which together with standards, were placed in a polyethylene container. Under the irradiation conditions chosen, activation of the polyethylene is insignificant. Irradiation of the test samples and standards was carried out in a homogeneous stream of thermal neutrons. After irradiation, the radioactive isotopes were isolated on isotopic carriers (20-30 mg calculated as the metal for each element). Since there was only a limited amount of test material, the test elements were divided into two groups: Ba, Ni, Cu, Sb, Mo and Mn, Cd, As, Au, Sn. Methods were developed for separating these elements from beryllium and for their radiochemical purification. The basis of the method was extraction of the diethyldithiocarbamate complexes of the test elements in chloroform [4], during which barium and beryllium remain in solution.

Separation of Mn^{II}, Cd, Au, As, Sn^{IV} from Irradiated Beryllium, Their Separation, and Purification. Concentrated hydrochloric acid, Mn^{II}, Au, Cd, As, Sn^{IV} carriers, and the irradiated metallic beryllium were placed in an apparatus provided with a reflux condenser.

After the samples had dissolved, the diethyldithiocarbamate complexes of As, Au, Sn^{IV} were extracted from the solutions in 10-12 N HCl with chloroform. Mn^{II} and Cd were extracted with chloroform from 1 N HCl; these elements were then reextracted into dilute (1 : 3) nitric acid, after which cadmium disulfide and manganese dioxide were precipitated.

In order to separate As, Au, and Sn^{IV}, the chloroform extract was evaporated to dryness and the residue boiled with nitric acid. The dry residue was dissolved in concentrated hydrochloric acid and gold and arsenic

TABLE 1

Test micro-impurity	Original isotopes	Activation cross section for thermal neutrons, 10^{-24} cm^2	Distribution of the isotope, %	Reaction product	Half-life period	Calculated sensitivity of the determination of the impurity, g
Mn	Mn^{55}	12,7	100	Mn^{56}	2,7 Hr.	$0,9 \cdot 10^{-9}$
Cd	Cd^{114}	0,28	10	Cd^{115}	56 Hr.	$1,25 \cdot 10^{-6}$
As	As^{75}	4,2	100	As^{76}	26 Hr.	$2,5 \cdot 10^{-8}$
Au	Au^{197}	96	100	Au^{198}	65 Hr.	$8,6 \cdot 10^{-8}$
Sn	Sn^{120}	0,14	32	Sn^{121}	28 Hr.	$4,9 \cdot 10^{-7}$
Ba	Ba^{138}	0,5	71	Ba^{139}	84 Min.	$9,1 \cdot 10^{-8}$
Ni	Ni^{64}	2,6	1	Ni^{65}	2,6 Hr.	$6 \cdot 10^{-7}$
Cu	Cu^{63}	3,9	69	Cu^{64}	12,8Hr.	$4 \cdot 10^{-8}$
Sb	Sb^{121}	6,8	57	Sb^{122}	2,8 Min.	$1,35 \cdot 10^{-7}$
Mo	Mo^{98}	0,13	23	Mo^{99}	67 Hr.	$1,2 \cdot 10^{-6}$

sulfides precipitated with hydrogen sulfide. Tin was isolated as its sulfide from a solution which was 1 N with respect to hydrochloric acid.

The gold and arsenic sulfides were dissolved in concentrated HCl containing hydrogen peroxide. Gold was extracted from a solution 1 N with respect to hydrochloric acid by means of diethyl ether. After removal of the gold, the aqueous layer was acidified to 6-8 N HCl and the arsenic reduced with hypophosphite to its elemental form.

In order to obtain radiochemically pure preparations, in addition to the separation operations, tin was purified further by precipitation of cesium hexachlorostannate from 12 N hydrochloric acid in the presence of hydrogen peroxide, and by precipitation as tin sulfide from a weakly acid medium; cadmium was purified further by precipitation of ferric hydroxide with pure ammonia, precipitation of cadmium sulfide from a weakly acid medium, and precipitation of the double phosphate of cadmium and ammonia; arsenic was purified further by precipitation as magnesium and ammonium arsenate; while manganese was purified by precipitation of manganese and ammonium phosphate. Gold was purified from radioactive contamination during its separation without additional chemical operations.

Isolation of Ba, Ni, Cu, Sb, and Mo from Irradiated Beryllium Their Separation, and Purification. Of the isotopes isolated, the ones with the shortest half-life period were Ba^{139} (T = 85 min) and Ni^{65} (T = 2.7 hr). Accordingly, in the method used, provision was made for separating these metals first.

Into an apparatus (fitted with a reflux condenser) containing 10-12 N hydrochloric acid were placed nickel, copper, antimony, and molybdenum carriers, and the irradiated metallic beryllium. The solution obtained was diluted until it was 3 N with respect to hydrochloric acid, barium was then added, and isolated as its sulfate.

Prior to extraction of the diethyldithiocarbamate complexes of Ni, Cu, Sb, and Mn from 3 N HCl, into chloroform, the antimony was reduced with hydrazine hydrochloride. After extraction, the chloroform extract containing nickel, copper, antimony, and molybdenum was evaporated to dryness and boiled with concentrated nitric acid. The dry residue was dissolved in 4% ammonia. Nickel, copper, and molybdenum dissolved, while antimony remained in the residue.

Nickel was isolated by extracting it as its dimethylglyoxime complex into chloroform from a weakly ammoniacal medium.

Nickel was reextracted from the chloroform into 2 N hydrochloric acid, and was reprecipitated as nickel dimethylglyoximate.

Copper was isolated by adding hydrochloric acid to the solution to give a neutral reaction, and extracted as copper dimethylglyoximate with chloroform. Copper was reextracted from the chloroform into ammonia, and was reprecipitated as cupric hydroxide. Molybdenum was isolated as its sulfide from a weakly acid medium.

The residue remaining after dissolving the dry residue in 4% ammonia was dissolved in 12 N HCl, and antimony sulfide precipitated from a solution 2 N with respect to hydrochloric acid. Since the antimony sulfide

TABLE 2

Test element	Av. content of the impurity in 1g of metallic beryllium, g	Average value of the impurity content, %	Relative experimental error, %
Cu	$3,7 \cdot 10^{-5}$	$3,7 \cdot 10^{-3}$	± 8
Ni	$5 \cdot 10^{-5}$	$5 \cdot 10^{-3}$	± 6
Sb	$3 \cdot 10^{-8}$	$3 \cdot 10^{-6}$	±10
Mo	$1,23 \cdot 10^{-5}$	$1,23 \cdot 10^{-3}$	±10
Ba	$2 \cdot 10^{-5}$	$2 \cdot 10^{-3}$	± 4
Mn	$4 \cdot 10^{-7}$	$4 \cdot 10^{-5}$	±10
Cd	$2,8 \cdot 10^{-6}$	$2,8 \cdot 10^{-4}$	± 3
Sn	$5,3 \cdot 10^{-5}$	$5,3 \cdot 10^{-3}$	±10
Au	$3,7 \cdot 10^{-8}$	$3,7 \cdot 10^{-6}$	±47**
As	$2,7 \cdot 10^{-7}$	$2,7 \cdot 10^{-5}$	± 6

* The error was calculated either by the mean square method, or mean statistical, depending on the number of samples analyzed.

** The comparatively large relative error is the result of uneven distribution of gold as an impurity in the test samples

precipitate contained traces of molybdenum, while the molybdenum precipitate contained traces of antimony, to separate these elements from each other, the precipitates were combined and washed with hot 6 N HCl. The antimony dissolved while the molybdenum remained in the precipitate. Antimony sulfide was precipitated from a weakly acid medium with hydrogen sulfide.

For obtaining radiochemically pure preparations, the following additional purification operations were used: for purifying barium, its sulfate was fused with a mixture of soda and potassium carbonate and after leaching with water, barium carbonate was precipitated; it was then precipitated with ferric hydroxide using pure ammonia, and finally precipitated as barium chromate; antimony was purified by extraction as quinquevalent antimony from 12 N hydrochloric acid with isopropyl ether, and precipitation as antimony sulfide from 2 N HCl after removal of the ether and precipitation as metaantimonic acid; molybdenum was purified by extracting it from 5 N hydrochloric acid in the presence of hydrazine hydrochloride, with subsequent reextraction into water and precipitation as molybdenum sulfide. Nickel and copper were purified from radioactive contamination without additional chemical purification. The standards of the test elements were purified from radioactive contamination in the same way as the test samples.

Target Measurement and Treatment of Results. The test element and its standard were placed on the targets used for measurement in the same gravimetric form. The amount of material on the targets and the measurement conditions were standardized, so that there was no need for applying corrections for self-absorption and self-scattering.

A MST-17 torsion counter in a B-2 setup was used for measuring the activity. In order to check on the radioactive purity of the elements isolated, decay curves were taken, and, when it was possible, absorption curves in aluminum were also taken. Identification of the preparations isolated showed that the techniques adopted enable one to obtain the test elements with the requisite radioactive purity.

After the activity measurements, the exact amount of material placed on the target was determined, after drying it or after ignition under definite conditions. For this purpose, gold sulfide was calcined at a temperature of 600° to the metal, while tin sulfide was converted into its dioxide at 600°; the magnesium and ammonium arsenate compound, the double phosphate of manganese and ammonium, and the double phosphate of cadmium and ammonium were calcined at 800° to give the compounds $Mg_2As_2O_7$, $Mn_2P_2O_7$, $Cd_2P_2O_7$.

Barium chromate was brought to constant weight at 600°, while nickel dimethylglyoximate and cupric hydroxide were ignited at 800° to give the oxides NiO and CuO. Molybdenum sulfide was calcined at 500° to MoO_2, and the precipitate of metaantimonic acid to Sb_2O_4 at 800°. Quantitative yields of the elements after separation and purification amounted to 60-80 %.

The activity of the elements in samples of the test material and in a standard sample at a definite time were found from the activity measurements.

The amount of an impurity in a test sample (X) was determined by means of the formula

$$X = \frac{Bma}{A_e M} \cdot \frac{A_x}{b},$$

where A_e is the activity of the element in the standard target referred to a definite time, A_x is the activity of the element in a target of the test sample referred to the same time, M is the amount of carrier added to the standard sample, B is the amount of carrier added to the test sample, a is the weight of sample in the standard target, b is the weight of material in a target with test sample, and m is the amount of material in the standard sample.

The formula was derived on the assumption that the impurity content (X) and the amount of material in test samples (m) is negligibly small compared with the amounts of carriers introduced M and B.

Results of the analysis of metallic beryllium for its content of Ba, Ni, Cu, Sb, Mo, Mn, Cd, As, Au, Sn present as impurities are given in Table 2.

The amount of gold and antimony present as impurities in one gram of metallic beryllium was lower than the calculated sensitivity of determination, by 2.3 times in the case of gold and 4.5 times in the case of antimony. As a result, the activity of antimony and gold targets, as a rule, did not exceed 50-100 impulses per minute against the background at the beginning of activity measurements.

So that the small number of impulses measured did not affect the accuracy of the determination of gold and antimony, the time for which the targets were measured was increased so that the statistical count error did not exceed 3%.

L. S. Chikisheva, M. A. Presnyakova, E. Shamonina, and P. P. Shevchenko took part in the work.

SUMMARY

Methods have been developed for the separation of beryllium, barium, nickel, copper, antimony, molybdenum, manganese, cadmium, gold, tin, and arsenic. It has been established that As, Au, Sn^{IV}, Ni, Cu, Sb^{III}, Mo can be extracted as their diethyldithiocarbamate complexes from 10-12 N HCl with chloroform. It has been found that in order to extract the diethyldithiocarbamate complex of antimony completely into the chloroform, the antimony must be reduced beforehand with hydrazine hydrochloride.

A radioactivation method has been developed for the determination of Ba, Ni, Cu, Sb, Mo, Mn, Cd, Sn, Au, and As present as impurities in metallic beryllium.

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RADIOACTIVATION DETERMINATION OF IMPURITIES IN HIGH PURITY THALLIUM

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Increasing the sensitivity of the determination of impurities in semiconducting materials is one of the most important problems of analytical chemistry. One of the highly sensitive methods of analysis which has been successfully used for the analysis of semiconductors both in the USSR and abroad, is radioactivation analysis [1-6]. The method consists essentially or irradiating the test material with a stream of slow neutrons, the interaction of which with microamounts of impurities leads to the formation of the corresponding radioisotopes; their activity is proportional to the mass of the test element.

Deuterons, α-particles, protons, and γ-rays are also used for the purposes of radioactivation analysis, but to a much lesser extent than neutrons. Test samples are usually irradiated in a nuclear reactor.

The use of neutron streams with an intensity of about $10^{12} - 10^{13}$ neutrons/cm^2/sec, and a sample weight of about 1 g, permits determination of a large number of elements with a sensitivity of $10^{-6} - 10^{-8}$ % [4]. For quantitative determination of the impurities, standards are used which contain known amounts of the test elements, and which are irradiated under the same conditions as those used for the samples.

The expenditure of a large amount of time in chemical separation, and the impossibility of identifying radioisotopes which have similar half-life periods without measuring the energy of their β-particles, complicate the use of the radiochemical variant of the method in a number of instances.

The use of a γ-scintillation spectrometer makes it possible to avoid these difficulties, as long as the sample, in which it is desired to determine the impurities, does not emit γ-rays, or the half-life period of the radioisotopes of the macrocomponent is so small, that by the time measurements are started, they have completely decayed. Examples of materials which can be analyzed without chemical separation, are silicon, graphite, thallium, and some other semiconducting materials.

The negligible self-absorption of γ-rays in the sample makes preparation of the samples for measurement simple.

The principle of the method consists in recording the γ-radiation emitted by the radioactive isotopes of the test elements by means of a detector, consisting of a NaI(T1) crystal (d = 30 mm, h = 20 mm) and a FÉU-S photomultiplier in a lead chamber. The collimators are located within the protective chamber. The spectrum impulses from the photomultiplier pass through a linear accelerator and discriminator into a fifty channel amplitude analyzer. The recording of the signals on the analyzer tube permits a record of the spectrum to be obtained on a linear scale. A so-called "circle–point" system is used in the memory setup. The rays of the cathode ray tube are turned round a point raster, the geometrical location of the irradiating points in the upper part of the raster is the spectrum to be measured.

The use of a γ-scintiallation spectrometer makes it possible to carry out both a qualitative determination of the impurities on the basis of one or more photo peaks, corresponding to the photoelectric absorption of the characteristic γ-rays, and a quantitative determination on the basis of the area or the height of the photo peaks, after taking into account the efficiency of the crystal for the various energies of the γ-rays, or by using standards. Additional identification is carried out by measuring the half-life period on the basis of the rate at which the value of the photo peaks falls off.

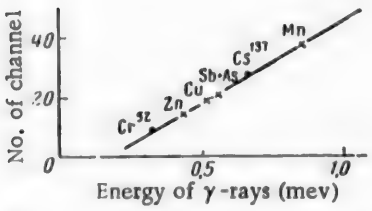

Fig. 1. Calibration curve of the spectrometer.

We have carried out some work on the determination of Mn, Zn, Cu, As, and Sb present as impurities in four samples of metallic thallium, using a fifty channel γ-scintillation spectrometer, without preliminary chemical separation. An aliquot (about 0.5 g) of a sample and the standards in the form of microamounts of the salts of the test elements, were placed in a quartz weighing bottle, preliminary treated with hot aqua regia and then washed with water, ethanol, and ether; the weighing bottles were wrapped in aluminum foil, placed in aluminum cases and irradiated with a neutron stream ($f = 0.87 \times 10^{13}$ neutrons/cm^2/sec) for 20-48 hours. After irradiation, the thallium sample was removed from the weighing bottle, pickled with concentrated hydrochloric acid, washed three times with water, ethanol, and ether; it was then transferred to a small test tube and used for measurements on a γ-spectrometer.

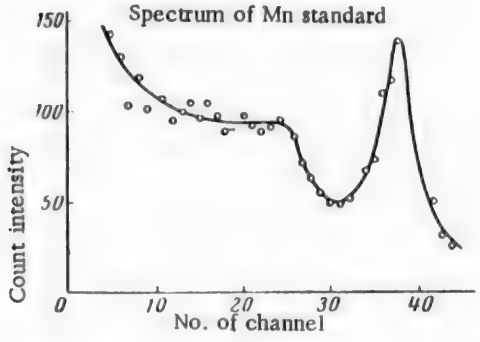

Fig. 2. Spectrum of the manganese standard.

The microamounts of the standards were washed out of the weighing bottles with 0.6 N hydrochloric acid, and carriers of the corresponding elements in amounts of 5-10 mg were added to the solution; they were then subjected to several purification operations to free them from contaminating impurities, mainly sodium.

In order to purify the manganese standard, it was precipitated with ferric hydroxide which was added to the solution containing the manganese; manganese dioxide was then precipitated twice with $KClO_3$, after which the double phosphate of ammonium and manganese was precipitated; finally, the latter, after calcining at 800° for 15 min, was weighed as manganese pyrophosphate.

The copper standard was purified by precipitating the copper as sulfide and thiocyanate. The thiocyanate precipitate was washed three times with water, ethanol, and ether, and finally dried and weighed.

The zinc standard was purified by precipitating it twice as zinc thiocyanomercuriate, which, after washing with water, ethanol, and ether, was weighed. The following purification operations were carried out on the antimony standard: precipitation as the sulfide and as metaantimonic acid. The precipitate obtained was washed with water, ethanol, and ether, it was then placed in a porcelain crucible, calcined to Sb_2O_4, and weighed.

The arsenic standard was purified by precipitation as its sulfide, followed by reduction of arsenic to the elemental state with sodium hypophosphite; the precipitate was washed three times with water, ethanol, and ether, dried and weighed.

The tared residues of the purified preparations of the standards were transferred to small test tubes and then measurements carried out on them.

An energy calibration of the analyzer scale was carried out prior to commencing measurements on the γ-spectrometer. Calibration was carried out using the radioactive isotopes Cs^{137} (E_γ = 0.66 Mev) and Cr^{52} (E_γ = = 0.32 Mev). In Fig. 1 is shown the calibration curve for the spectrometer constructed by means of Cs^{137} and Cr^{52}, the energies of the photo peaks of the Mn, Zn, Cu, As, and Sb standards are included. The spectra of the

Sample No.	Impurities determined, %				
	Mn	Cu	Zn	Sb	As
0	$2{,}9\cdot10^{-7}$	$3\cdot10^{-7}$	—	$<4\cdot10^{-6}$	$2\cdot10^{-6}$
1	$1{,}3\cdot10^{-7}$	$1\cdot10^{-7}$	$4\cdot10^{-5}$	$<9\cdot10^{-6}$	$5\cdot10^{-6}$
2	$<4\cdot10^{-6}$	$1{,}8\cdot10^{-7}$	$1\cdot10^{-5}$	$<2\cdot10^{-6}$	$1\cdot10^{-6}$
145	$<4\cdot10^{-6}$	$<1\cdot10^{-7}$	—	$<2\cdot10^{-6}$	$1\cdot10^{-6}$

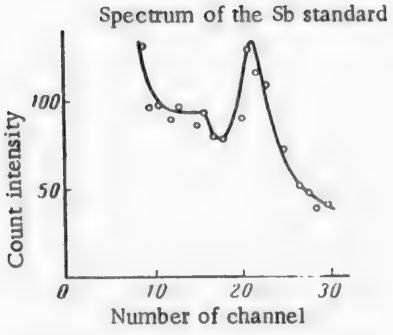

Fig. 3. Spectrum of the antimony standard

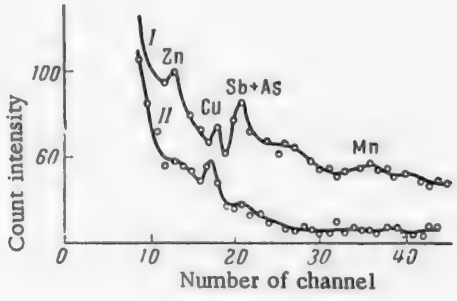

Fig. 4. Spectrum of thallium samples. 1) Spectrum of sample No. 1; II) spectrum of sample No. 2.

manganese and antimony standards are shown in Figs. 2 and 3. Spectra of test samples of thallium (Nos. 1 and 2) are shown in Fig. 4. Photo peaks corresponding to Mn, Zn, Cu, and As + Sb are evident on Fig. 4. The photo peak in channel 23 could be the total photo peak of the isotopes As^{76} (E_γ = 0.56 Mev) and Sb^{122} (E_γ = 0.57 Mev). For identification purposes the decay curve of this photo peak was taken. The half-life period proved to be close to that of the period of As^{76} (T = 26 hr). Consequently, the area of the photo peak was subsequently ascribed to As^{76}, while the Sb content indicated in the table is only the upper limit of the concentration of the impurity which can be determined in the given sample. The sharp rise in the curve in the initial section of the spectra is determined by the x-ray radiation of Tl^{204} and partially by the Compton contribution of the impurity elements. The spectra of samples Nos. 0 and 145 are shown in Fig. 5. The absence of Zn photo peaks is explained by the fact that the sharp rise in the curve, and the very low Zn content do not permit even an approximate evaluation of its content in these samples. The lowest curve in Fig. 5 is the spectrum of the background.

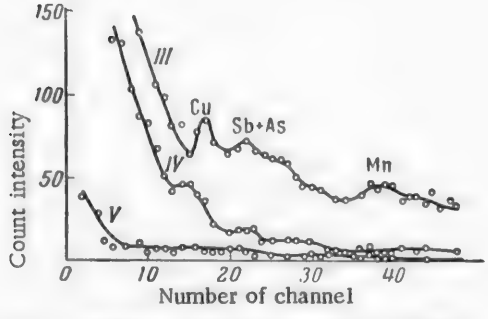

Fig. 5. Spectra of thallium samples. III) Spectrum of sample No. 0; IV) spectrum of sample No. 145; V) spectrum of the background.

Quantitative determination of the impurities was carried out by comparing the areas or the heights of the photo peaks of the test sample and of the standards, referred to the same measurement time. Correction for the geometry was not introduced, since the samples and the standards were measured under identical conditions.

The mass of the test impurities was calculated by means of the equation $m_{sample} = m_{standard} \cdot S_{sample}/S_{standard} \cdot K$, where m_{sample} is the mass of the test element; $m_{standard}$ is the mass of the standard; $m_{sample}/S_{standard}$ is the ratio of peak areas or peak heights of the photo currents; K is a correction for the chemical yield of the standard.

After calculating the absolute mass of the impurity, its content in the sample was calculated (in %).

Results of the analysis of thallium samples for the impurities listed above are given in the table.

An examination of the table shows that the Sb content of all four samples, and the Mn content of two of them, is less than the sensitivity of the determination. Some ideas relating to an evaluation of the sensitivity of the determination of Sb have been described above; while an evaluation of the sensitivity of Mn determination in samples Nos. 2 and 145 was carried out by the method of additions.

SUMMARY

A method has been developed for the determination of Mn, Cu, Zn, As, and Sb present as impurities in high purity thallium.

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CHEMICOSPECTROGRAPHIC DETERMINATION OF IMPURITIES IN THORIUM AND ITS COMPOUNDS

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Some information on the determination of impurities in pure metallic thorium and its compounds has been published [1-6]. Chemical analytical methods are very complicated [2, 3]. Spectrographic analysis of thorium is also difficult because of the high degree of complexity of the emission spectrum of the base. Accordingly, in order to determine impurities with a high degree of sensitivity, either carrier methods (e. g., Ga_2O_3), or spectrographs with a high resolving capacity [1, 7, 8], or an evaporation method are used [9].

During chemicospectrographic determination of impurities in thorium, the impurities are concentrated chemically and then determined spectrographically. The characteristics of the method used are the same as those described previously [10, 11]. Concentration of the impurities is carried out by almost complete removal of the base (thorium) by two techniques: by precipitation of thorium as its oxalate or in the form of its peroxide. A concentrate of the impurities is prepared from the mother liquor and beryllium oxide added as a base. This permits determination of a large number of elements with a high sensitivity on a spectrograph with average dispersion, since the spectrum of the concentrate of the impurities is freed from the thorium lines (see Figs. 1 and 2).

A Chemicospectrographic Method Involving Removal of Thorium as Its Oxalate. Thorium is removed from the impurities by precipitating it as the oxalate from a weakly nitric acid medium. The aqueous solution containing the impurities is evaporated after addition of beryllium nitrate, it is then treated with ammonia, and, after evaporating the solution, and calcining the residue, a powdered concentrate of the impurities is obtained on a beryllium oxide base in a glass-like form. The enrichment coefficient of the impurities in the concentrate is 20-30. The impurities in the concentrate are determined spectrographically, using standards also prepared on a beryllium oxide base. The spectra are excited in a dc arc between carbon electrodes, and are photographed on a medium dispersion spectrograph. This method permits determination of the following 18 elements present as impurities in thorium, by means of one spectrogram: Mg, Ca, Ba, Al, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Sn, Sb. Results on the sensitivity of the method are given in Table 1. The accuracy of the method is on the average ± 20% (relative).

Concentration of the Impurities. Precipitation of thorium by oxalic acid is a fairly selective method, and was accordingly used for concentrating the impurities during their determination in thorium. According to published results [2], it is possible to separate thorium from the alkali and alkaline earth metals, Fe, Al, Cr, Co, Ni, Zn, Be, Ga, Ti, Zr, and U. The following conditions were chosen for precipitating the oxalate, these conditions ensuring fairly complete separation of thorium, and minimum coprecipitation of impurities: a) precipitation is carried out in a weakly acid medium (1 N HNO_3) from hot solution by gradual addition of precipitant while the solution is stirred; b) the precipitate plus mother liquor are kept on a water bath for recrystallization and self-purification; c) during precipitation, oxalic acid amounting to 80% of the stoichiometric amount is first added, while after a certain time the remainder of the precipitant is added in twofold excess. It was found that when this method of precipitation was used—by addition of the oxalic acid in two lots—the thorium oxalate precipitate

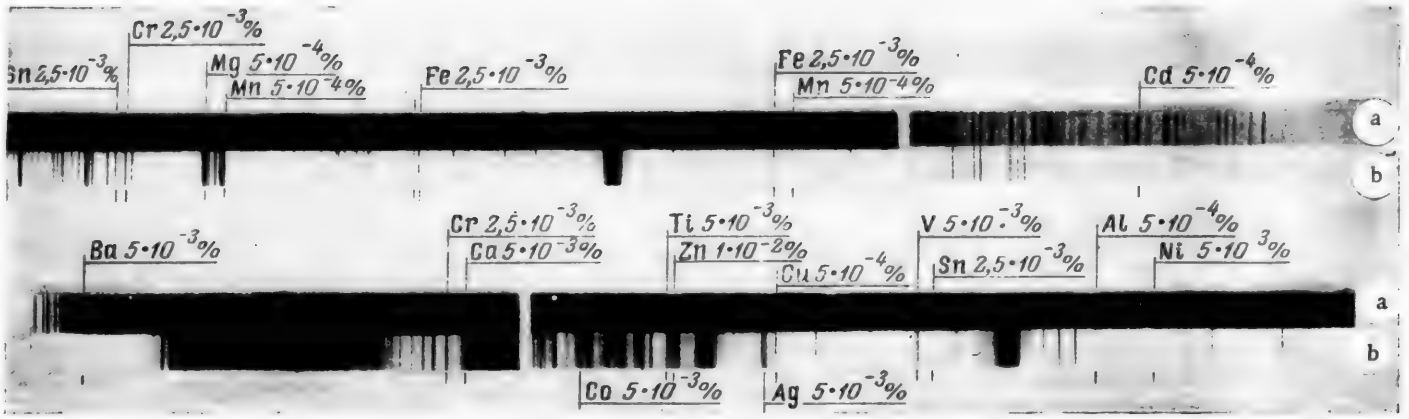

Fig. 1. Spectrograms: (a) sample of thorium (as ThO_2); (b) concentrate of the impurities obtained from the same sample on a BeO base. The impurities were added artificially; concentration was carried out by the oxalate method, the enrichment coefficient being K = 9.

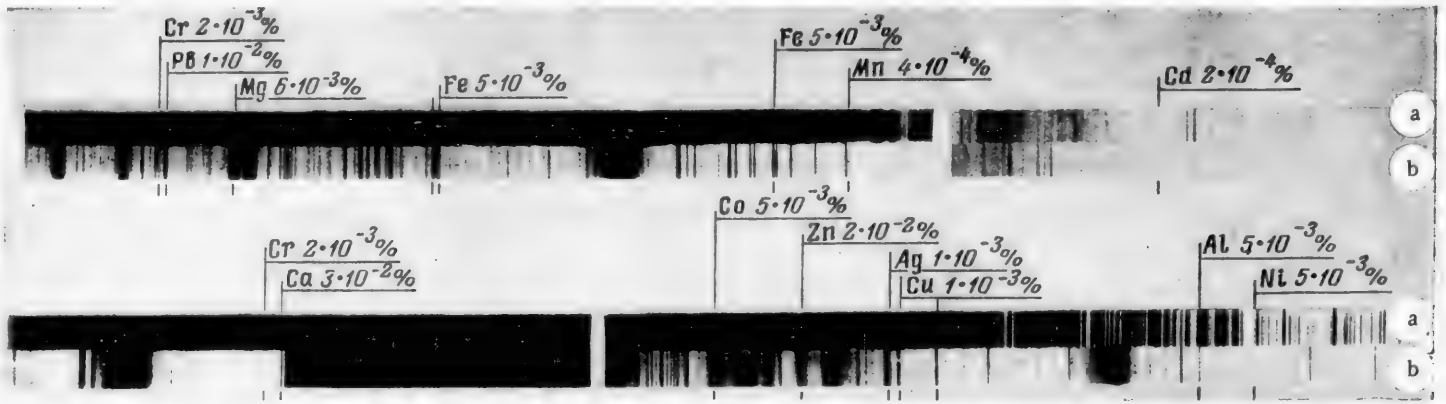

Fig. 2. Spectrograms: (a) thorium sample (as ThO_2); (b) concentrate of the impurities from the same sample on a BeO base. The impurities were added artificially; concentration was carried out by the peroxide method, the enrichment coefficient being K = 2.5.

TABLE 1

Sensitivity of the Determination of Impurities in Thorium (K is the enrichment coefficient)

Element and analytical line	Precipitation method	
	oxalate with K = 20	peroxide with K = 5
Mg 2802,7	$2 \cdot 10^{-5}$	$6 \cdot 10^{-5}$
Ca 4226,7	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Ba 4934,1	$2 \cdot 10^{-4}$	$6 \cdot 10^{-4}$
Al 3082,2	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Ti 3349,0	$1 \cdot 10^{-4}$	
V 3184,0	$5 \cdot 10^{-5}$	
Cr 2835,6	$5 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
Mo 2816,2	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Mn 2576,1	$1 \cdot 10^{-5}$	$4 \cdot 10^{-5}$
Fe 2599,4	$5 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
Co 3412,6	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Ni 3050,8	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Cu 3247,5	$1 \cdot 10^{-5}$	$4 \cdot 10^{-5}$
Ag 3280,7	$2 \cdot 10^{-5}$	$6 \cdot 10^{-5}$
Zn 3345,0	$5 \cdot 10^{-4}$	$2 \cdot 10^{-3}$
Cd 2288,0	$5 \cdot 10^{-6}$	$2 \cdot 10^{-5}$
Sn 2840,0	$1 \cdot 10^{-4}$	
Sb 2598,1	$2 \cdot 10^{-4}$	
Pb 2833,1		$4 \cdot 10^{-4}$

obtained was very compact, almost half the volume of the precipitate obtained when all the oxalic acid is added at once. The amount of thorium left in the solutions when the precipitation conditions described above were used, as determined from data on the solubility of thorium oxalate [12] and according to experiments which we carried out, was very insignificant—not more than 1 mg in 100 ml of solution (usually 0.5-0.6 mg Th)—and did not interfere with subsequent spectrographic determination of the impurities in the concentrate. Published results [1] on the quantitative removal of traces of elements during precipitation of thorium oxalate were checked experimentally.

Various amounts of standard solutions of the impurity elements (from 1×10^{-4} to 1×10^{-1}% of each elements, calculated as the metal) were added to preparations of thorium nitrate* which had been specially purified and checked for the absence of impurities. These mixtures were taken through all the analytical stages involving removal of thorium as the oxalate. The distribution of the impurity elements between the solution and precipitate was established by analyzing each phase. For this purpose, the mother liquor was separated from the precipitate after the first precipitation, while the precipitate was calcined at 300°, dissolved in nitric acid, and then reprecipitated with oxalic acid. The mother liquor left from the first precipitation (the main impurity concentrate) and the solution left after the reprecipitation of the oxalate, were each analyzed spectrographically by the method described below. The balance for the distribution of the elements between the phases was then compiled. On the basis of these experiments, and also on the basis of experiments carried out for checking the analytical accuracy on synthetic mixtures (the object of the work) described below, it was established that the following elements, present as impurities, are almost completely extracted in the main impurity concentrated: Mg, Al, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn, Sb.

Traces of Ag were found to be concentrated in the nitric acid mother liquor. Under the conditions used, in the presence of traces of Cl^-, traces of Ag are completely concentrated for contents of less than 1×10^{-3} % Ag. Traces of Ca and Ba are concentrated completely when their contents are less than 1×10^{-2} %.

Completeness of extraction of traces of elements in the concentrate is 85-100% (Table 2). Quantitative extraction of a number of other elements (Fe, Co, Cr) was also checked chemically.

The efficiency of the removal of thorium and the concentration of the impurities is illustrated in Fig. 1, where a comparison is made of the spectrogram of a synthetically prepared sample of thorium dioxide, and that of a concentrate of the impurities obtained from the same sample.

Experimental Procedure. Preparation of the Chemical Concentrate. A three gram sample of metallic thorium is dissolved in aqua regia in a 300 ml quartz conical flask. Marks corresponding to volumes of 100 and 150 ml should be made on the flask. Dissolution is carried out carefully at first and then with vigorous heating. The black or yellow precipitate formed [13] should dissolved completely. The solution is evaporated almost to dryness, nitric acid being added to convert all the salts into the nitrates, 8 ml of concentrated nitric acid is then added and the volume of the solution diluted to 100 ml with water, i. e., until the HNO_3 concentration is about 1 N HNO_3. The solution is heated, and to the hot liquid is added slowly, with stirring, a hot 10% solution of oxalic acid which is measured out accurately at the rate of 2.64 g $H_2C_2O_4 \cdot 2H_2O$ per 3 g of thorium metal.

* Purification was carried out by reprecipitating thorium oxalate until there were no impurities in the concentrate prepared from the mother liquor on a beryllium oxide base. The concentrate was analyzed spectrographically.

TABLE 2

Enrichment of Traces of Impurities in the Concentrate during Precipitation of Thorium

Elements (impurities)	Completeness of extraction during separation by precipitation (mean value), %	
	oxalate	peroxide
Mg	98	92
Ca	85	94
Ba	90	96
Al	99	90
Ti	99	—
V	95	—
Cr	98	98
Mo	85	97
Mn	95	94
Fe	100	96
Co	99	98
Ni	99	98
Cu	95	95
Ag	90	92
Zn	100	92
Cd	95	94
Sn	100	—
Sb	95	—
Pb	—	96

The solution plus the precipitate is kept for four hours on a water bath, and the second portion of the oxalic acid, amounting to 3.96 g per 3 g of Th, added in the same way. Water is added to bring the volume up to 150 ml, and the solution plus precipitate kept for one hour on the water bath, and for three hours at room temperature. An aliquot of the mother liquor (120 ml) is then carefully decanted, without disturbing the precipitate, into a beaker on which the volume has been marked out. The liquor which has been poured off is evaporated in a tared quartz basin, to which a solution of spectrographically pure beryllium nitrate containing 100 mg Be has been added. Three ml of concentrated HNO_3 is added, and the liquor evaporated to dryness, and calcined at 200-300° to remove excess oxalic acid. The residue is dissolved in 3 ml HNO_3 and is evaporated to a sirupy state. Beryllium hydroxide is precipitated by adding 25% ammonia with stirring, the precipitate is dried and calcined at 250-300° until all the ammonium nitrate has been removed, and then calcined at 500° for 30 min. The powdered concentrate obtained is weighed in order to determine the enrichment coefficient, it is then ground and analyzed spectrographically. Chemical concentrates of the impurities are made in the same way during the analysis of thorium compounds which are converted into the nitrate. The control test is taken through all the stages of the analysis using all the reagents.

Quartz vessels are used. The reagents—hydrochloric and nitric acids, ammonia, and water—are distilled in quartz vessels. Oxalic acid is purified by recrystallization. The beryllium nitrate solution which has a concentration of 40-45 mg Be/ml is prepared from beryllium acetate which has been purified by extraction with chloroform [14].

Note. Pb and Bi present as impurities are not completely concentrated during separation of thorium oxalate; they can be determined spectrographically after removal by extraction with sodium diethyldithiocarbamate and with dithizone in a separate aliquot of sample.

Spectrographic Determination of Impurities. Determination of impurities on a beryllium oxide base has been outlined in detail in another paper [14]. The spectra are photographed on a ISP-22 spectrograph, the slit width being 10 μ; a two stage attenuator with a relative percentage transmission of approximately 10 : 1 is fitted in front of the slit. The spectra are excited in a dc arc at a current strength of 10 amp. The exposure time is 2 min. The lower electrode (anode) has an opening with a diameter of 4 mm and a depth of 6 mm, while the upper electrode is a rod sharpened to a cone. The weight of the powdered concentrate or standards, on a BeO base, fed into one of the electrodes, is 50 mg. The powder in the opening of the electrode is moistened with two drops of a 20% alcoholic solution of Bakelite and is dried on a hot plate. Calibration curves are constructed within the coordinates (log I, log C), the background being taken into account, where I is the line intensity, and C is the concentration. The results obtained from the calibration curve are divided by the enrichment coefficient of the impurities in the concentrate in order to obtain their percentage contents in the original sample.

Chemicospectrographic Method with Separation of Thorium as its Peroxide. The given method differs from the preceding method by the technique used for concentrating the impurities. Thorium is removed from impurities by precipitating it with hydrogen peroxide from a weak nitric acid solution, and the precipitate centrifuged. After reprecipitation, the combined solutions are evaporated after addition of beryllium nitrate, the mixture is treated with ammonia and then dried; after calcination, a powdered concentrate of the impurities is obtained on a beryllium oxide base in a glass like form. The enrichment coefficient of the impurities in the concentrate is 2.5-5. The spectrographic analysis of the concentrate is carried out in the same way as that described in the previous section. By this method the content of the following 15 elements, present as impurities, is determined: Mg, Ca, Ba, Al, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb. The sensitivity of the method is given in Table 1. The accuracy of the method is characterized by an average relative error of ±20%.

Concentration of the Impurities. For separating thorium quantitatively and concentrating the impurities, the very selective reaction of precipitating thorium with hydrogen peroxide is used [1, 2, 15, 16]. According to

TABLE 3

Results of the Analysis of Synthetic Mixtures (Thorium removed as the peroxide)

Elements	Impurity content in percent, with respect to Th					
	Mixture No. 8		Mixture No. 9		Mixture No. 10	
	added	found	added	found	added	found
Mg	$7,5 \cdot 10^{-4}$	$6,0 \cdot 10^{-4}$	$7,5 \cdot 10^{-4}$	$6,0 \cdot 10^{-4}$	$2,0 \cdot 10^{-4}$	$1,7 \cdot 10^{-4}$
Ca	$1,0 \cdot 10^{-3}$	$1,1 \cdot 10^{-3}$	$1,0 \cdot 10^{-3}$	$9,0 \cdot 10^{-4}$	$5,0 \cdot 10^{-4}$	$4,0 \cdot 10^{-4}$
Ba	$2,0 \cdot 10^{-3}$	$3,2 \cdot 10^{-3}$	$2,0 \cdot 10^{-3}$	$3,0 \cdot 10^{-3}$	$1,0 \cdot 10^{-3}$	$1,2 \cdot 10^{-3}$
Al	$7,0 \cdot 10^{-4}$	$7,5 \cdot 10^{-4}$	$7,0 \cdot 10^{-4}$	$7,5 \cdot 10^{-4}$	$3,5 \cdot 10^{-4}$	$4,5 \cdot 10^{-4}$
Ti	$2,0 \cdot 10^{-3}$	$2,4 \cdot 10^{-3}$	$2,0 \cdot 10^{-3}$	$2,6 \cdot 10^{-3}$	$1,0 \cdot 10^{-3}$	$1,0 \cdot 10^{-3}$
V	$6,0 \cdot 10^{-4}$	$7,0 \cdot 10^{-4}$	$6,0 \cdot 10^{-4}$	$7,0 \cdot 10^{-4}$	$3,0 \cdot 10^{-4}$	$2,5 \cdot 10^{-4}$
Cr	$4,7 \cdot 10^{-4}$	$3,7 \cdot 10^{-4}$	$4,7 \cdot 10^{-4}$	$4,1 \cdot 10^{-4}$	$2,3 \cdot 10^{-4}$	$1,9 \cdot 10^{-4}$
Mo	$4,0 \cdot 10^{-4}$	$4,0 \cdot 10^{-4}$	$4,0 \cdot 10^{-4}$	$4,5 \cdot 10^{-4}$	$2,0 \cdot 10^{-4}$	$2,1 \cdot 10^{-4}$
Mn	$6,5 \cdot 10^{-5}$	$5,0 \cdot 10^{-5}$	$6,5 \cdot 10^{-5}$	$5,5 \cdot 10^{-5}$	$3,2 \cdot 10^{-5}$	$3,0 \cdot 10^{-5}$
Fe	$4,0 \cdot 10^{-4}$	$6,6 \cdot 10^{-4}$	$4,0 \cdot 10^{-4}$	$7,6 \cdot 10^{-4}$	$2,0 \cdot 10^{-4}$	$1,8 \cdot 10^{-4}$
Co	$1,2 \cdot 10^{-3}$	$1,7 \cdot 10^{-3}$	$1,2 \cdot 10^{-3}$	$1,6 \cdot 10^{-3}$	$6,0 \cdot 10^{-4}$	$6,0 \cdot 10^{-4}$
Ni	$4,0 \cdot 10^{-4}$	$6,0 \cdot 10^{-4}$	$4,0 \cdot 10^{-4}$	$7,0 \cdot 10^{-4}$	$2,0 \cdot 10^{-4}$	$2,7 \cdot 10^{-4}$
Cu	$4 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$2 \cdot 10^{-5}$
Ag	$6 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$1,0 \cdot 10^{-4}$	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$
Zn	$6,0 \cdot 10^{-3}$	$8,5 \cdot 10^{-3}$	$6,0 \cdot 10^{-3}$	$9,5 \cdot 10^{-3}$	$3,0 \cdot 10^{-3}$	$4,0 \cdot 10^{-3}$
Cd	$2,0 \cdot 10^{-5}$	$2,5 \cdot 10^{-5}$	$2,0 \cdot 10^{-5}$	$2,5 \cdot 10^{-5}$	$1,0 \cdot 10^{-5}$	$6 \cdot 10^{-6}$
Sn	$4,0 \cdot 10^{-4}$	$4,7 \cdot 10^{-4}$	$4,0 \cdot 10^{-4}$	$4,5 \cdot 10^{-4}$	$2,0 \cdot 10^{-4}$	$2,0 \cdot 10^{-4}$
Sb	$6,0 \cdot 10^{-4}$	$7,0 \cdot 10^{-4}$	$6,0 \cdot 10^{-4}$	$7,0 \cdot 10^{-4}$	$3,0 \cdot 10^{-4}$	$2,5 \cdot 10^{-4}$

published data, precipitation of thorium as its peroxide in neutral or weakly acid solution permits its separation from many foreign elements, and this method is recommended for determining thorium in ores with a complex composition [2, 3]. The composition and the nature of the thorium peroxide precipitate are strongly dependent on the precipitation conditions. In weakly acid media, a white, opaque, bulky precipitate is formed which has a variable composition, and which has only a very weakly expressed crystalline structure containing anions (NO_3^-, Cl^-, etc), and is strongly hydrated [1, 2]. In order to precipitate thorium completely and obtain a peroxide precipitate in a dense form, in which the minimum amount of impurities is entrained, the conditions usually recommended were chosen. Precipitation was carried out in a hot solution containing 5% NH_4NO_3, the original acidity of the solution being 0.1 N with respect to HNO_3. Acid concentrations greater than 0.3 N HNO_3 lead to some increase in the solubility of the precipitate. It should be borne in mind that during formation of thorium peroxide, an equivalent amount of acid is formed. After being allowed to stand, the thorium peroxide precipitate is removed by centrifugation from the mother liquor which contains the impurities. The volume occupied by the precipitate amounts to less than 10% of the total volume of solution.

For complete separation of the impurities, reprecipitation of the peroxide is specified. Under the experimental conditions, thanks to almost complete separation of thorium, only traces of thorium remain in the concentrate of the impurities, these traces being considerably lower than the permissible limits of spectrographic analysis (equal to about 1% Th in the weight of the concentrate).

A check was made on the distribution of the impurity elements between the phases, and on their extraction into the concentrate under the conditions of the method developed. Standard solutions of 15-22 elements, in amounts ranging from 10^{-2} - 10^{-3}% of each element with respect to thorium, were added to aliquots of specially purified thorium nitrate. The thorium peroxide was precipitated and then reprecipitated, and the impurity concentrate prepared on a beryllium oxide base by the technique described below. In order to determine the amount of the impurities entrained by the centrifuged precipitate of thorium peroxide, the latter was dissolved in a nitric acid solution, and the peroxide again precipitated, as a result of which a second concentrate of the impurities was obtained. The first concentrate (the principal) and the second (check) were analyzed spectrographically by the method developed. On the basis of the analytical results obtained, a comparison was made of all the elements added and found in each fraction. On the basis of several series of such experiments, it was established that the completeness of extraction of 15 impurity elements into the concentrate amounts to about 90-98%, as indicated in Table 2.

TABLE 4

Results of the Analysis of Synthetic Mixtures (Thorium removed as the peroxide)

Elements	Impurity content in percent, with respect to Th			
	Mixture No. 13		Mixture No. 28	
	added	found	added	found
Mg	$1{,}0\cdot10^{-2}$	$9{,}3\cdot10^{-3}$	$4{,}0\cdot10^{-3}$	$3{,}6\cdot10^{-3}$
Ca	$3{,}0\cdot10^{-2}$	$3{,}7\cdot10^{-2}$	$1{,}2\cdot10^{-2}$	$1{,}5\cdot10^{-2}$
Ba	$5{,}0\cdot10^{-2}$	$4{,}2\cdot10^{-2}$	$2{,}0\cdot10^{-2}$	$2{,}0\cdot10^{-2}$
Al	$5{,}0\cdot10^{-2}$	$6{,}8\cdot10^{-2}$	$2{,}0\cdot10^{-2}$	$1{,}7\cdot10^{-2}$
Cr	$2{,}0\cdot10^{-2}$	$1{,}7\cdot10^{-2}$	$8{,}0\cdot10^{-3}$	$8{,}4\cdot10^{-3}$
Mo	$1{,}0\cdot10^{-2}$	$1{,}4\cdot10^{-2}$	$4{,}0\cdot10^{-3}$	$4{,}2\cdot10^{-3}$
Mn	$4{,}0\cdot10^{-3}$	$3{,}5\cdot10^{-3}$	$1{,}6\cdot10^{-3}$	$1{,}3\cdot10^{-3}$
Fe	$2{,}0\cdot10^{-2}$	$2{,}1\cdot10^{-2}$	$1{,}2\cdot10^{-3}$	$1{,}2\cdot10^{-3}$
Co	$5{,}0\cdot10^{-2}$	$3{,}4\cdot10^{-2}$	$2{,}0\cdot10^{-2}$	$1{,}9\cdot10^{-2}$
Ni	$5{,}0\cdot10^{-2}$	$3{,}8\cdot10^{-2}$	$2{,}0\cdot10^{-2}$	$1{,}9\cdot10^{-2}$
Cu	$3{,}9\cdot10^{-3}$	$4{,}0\cdot10^{-3}$	$2{,}7\cdot10^{-3}$	$2{,}3\cdot10^{-3}$
Ag	$4{,}7\cdot10^{-3}$	$4{,}7\cdot10^{-3}$	$3{,}2\cdot10^{-3}$	$2{,}1\cdot10^{-3}$
Zn	$1{,}0\cdot10^{-1}$	$7{,}8\cdot10^{-2}$	$8{,}0\cdot10^{-2}$	$5{,}0\cdot10^{-2}$
Cd	$1{,}0\cdot10^{-3}$	$5{,}5\cdot10^{-4}$	—	—
Pb	$3{,}0\cdot10^{-2}$	$3{,}1\cdot10^{-2}$	$1{,}2\cdot10^{-2}$	$1{,}0\cdot10^{-2}$

Ti, V, Sn, and Sb are coprecipitated with thorium peroxide, and cannot be determined. The fact that almost complete concentration of traces of the elements is achieved, was also confirmed by analysis of synthetic mixtures (problem) during a check on the accuracy of the method (see below). The efficiency with which the base is removed, and the impurities concentrated, is illustrated by a comparison of the spectrograms of samples and concentrates in Fig. 2.

Experimental Procedure. Preparation of the Chemical Concentrate. An aliquot of thorium metal weighing 0.250 g is dissolved in aqua regia in a quartz beaker. Heating is continued until the black or yellow precipitate has dissolved. The solution is evaporated three times almost to dryness, nitric acid being added to convert the salts to nitrates. The dry salts are dissolved on heating in 3 ml of water to which 1 ml of 5 N HNO_3 has been added. Water is added to bring the volume up to about 40 ml, and 2 g of crystalline, spectrographically pure ammonium nitrate added. The weakly nitric acid solution obtained, which has an acidity of about 0.1 N HNO_3, is heated to 60-80°, and 10 ml of a 15% H_2O_2 solution added slowly, with stirring, until thorium peroxide has been completely precipitated. After standing for one hour, the solution is removed from the precipitate by centrifuging in a quartz test tube. The beaker walls are rinsed three times with 3 ml portions of 1% NH_4NO_3 solution. The thorium peroxide precipitate is dissolved in 7 N HNO_3, the solution is evaporated, and the peroxide reprecipitated under the conditions outlined above. The solutions separated from the precipitate are poured into a tared quartz basin, a solution of spectrographically pure beryllium nitrate containing 100 mg Be is added, and the liquid evaporated to a sirupy state. The hydroxides are precipitated with excess of 25% ammonia, they are dried and then calcined at 250-300° to remove the ammonium nitrate; they are finally calcined at 500° for 30 min. The concentrate of the impurities on a BeO base is weighed in order to determine the enrichment coefficient, and is then analyzed spectrographically. A blank test is carried out in parallel, the same reagents and identical conditions being used. All operations are carried out in quartz vessels. Water, acids, and ammonia are redistilled in quartz apparatus, as well as the hydrogen peroxide (under vacuum). Ammonium nitrate is prepared by neutralizing redistilled nitric acid with ammonia.

The spectrographic analysis is carried out by the technique outlined above.

The accuracy and reproducibility of the two variants described above for the chemicospectrographic method were checked by analyzing synthetic mixtures. The mixtures were prepared by addition to thorium nitrate preparations which had been purified beforehand by several reprecipitations (as the oxalate or peroxide, respectively), of standard solutions of 15-20 elements in amounts ranging from 10^{-3} to 10^{-5}% (with respect to thorium). The synthetic mixtures, as well as the thorium nitrate preparations used, were subjected to complete analysis by the appropriate method. Examples of the analyses of several mixtures are given in Tables 3 and 4.

SUMMARY

Two variants of a chemicospectrographic method for the determination of traces of impurities in thorium and its compounds have been developed. In the first of these variants, the impurities are concentrated by separating thorium as its oxalate from a weak nitric acid medium; the enrichment coefficient of the impurities is 20-30. In the second variant, the impurities are concentrated by separating thorium from a weak nitric acid medium in the form of its peroxide; the enrichment coefficient is 2.5-5. In both variants, the powdered concentrate obtained on a beryllium oxide base, after evaporating the solution of the impurities, is spectrographically analyzed; the spectra are excited in a dc arc and photographed on a quartz spectrograph having average dispersion.

Eighteen elements: Mg, Ca, Ba, Al, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Sn, Sb are determined simultaneously on one spectrogram when the first variant is used; while when the second variant is employed 15 elements can be determined: Mg, Ca, Ba, Al, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb.

Owing to removal of the thorium, and concentration of the impurities, the sensitivity with which they can be determined is correspondingly increased (to 10^{-4} - 10^{-5} %).

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A RAPID MICROMETHOD FOR THE DETERMINATION OF SULFUR IN MONOMERIC AND POLYMERIC ORGANIC COMPOUNDS IN THE PRESENCE OF HALOGEN, NITROGEN, AND THE ALKALI METALS

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A considerable number of articles have been published on the development of methods for the quantitative determination of sulfur in organic and inorganic compounds [1-11]. When halogens, nitrogen, and the alkali metals are also present, sulfur is determined titrimetrically [2-4, 6, 9] or gravimetrically [5]. The most suitable method from our point of view proved to be Boetius' method [4], which consists in combustion of an aliquot of the test compound in a flask filled with oxygen, followed by titration of the sulfuric acid formed by barium nitrate using sodium alizarinsulfonate (alizarin red S) as indicator.

Precipitation of barium sulfate under various conditions has been studied in detail by Geyer [1] who used a number of inorganic compounds. Boetius et al adopted Geyer's method for the analysis of organic compounds containing other elements (halogens, nitrogen, and the alkali metals) in addition to sulfur. When, however, we checked this method, it was found that Boetius' method as described did not contain sufficient detail (in particular, the weight of sample taken was not indicated), and accordingly we did not obtain positive results.

In the work described here we studied the analytical stages separately, and we have given a detailed description of a technique for the quantitative determination of sulfur in monomers and polymers containing halogens, nitrogen, and the alkali metals.

We found out that readily reproducible results are obtained when the test mixture is completely free from hydrogen peroxide which is normally used for oxidizing the sulfur oxides formed to SO_3; complete removal of hydrogen peroxide was effected only by evaporating the contents of the flask in the presence of platinum black until the moist salts were obtained. Evaporation to the moist salt state has the added advantage that it is then possible to establish the desired ratio of the organic and aqueous phases (1 : 1) accurately [1].

By modifying individual details in the analytical procedure and the ratios of the reagents, we obtained completely satisfactory results for materials containing from 2 to 40% of sulfur (see Table 1).

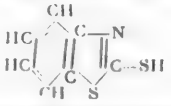
Table 2 contains results for the determination of sulfur in polymeric compounds when the flask combustion method was used, and also results obtained by the hydrogenation method [12].

Experimental. Aliquots of the test material were burnt in 250 ml conical flasks filled with oxygen. The apparatus and technique of the oxygen flask combustion method have been described in detail in the paper by Sokolova et. al., [13].

* 2-3 drops of formalin can be added instead of platinum black.

TABLE 1

Sample Weight 2-6 mg; 5 ml acetic acid (2 : 3); 1 ml of 0.5 N NaOH; 3 drops of a 0.1% aqueous solution of sodium alizarinsulfonate; ethanol : water = 1 : 1; total volume 20 ml

Test material	Sample wt., mg	0.02 N $Ba(NO_3)_2$ used, ml	S content, % found	S content, % calc.
Ditozylmonochlorohydrin of xylylthane $CH_2Cl \cdot CH-(CHO_3SO_7H_7)_2 \cdot CH_2$	6,210	2,68	13,84	13,91
	5,790	2,51	13,90	
Diphenylthiourea $S=C(NHC_6H_5)_2$	3,920	1,72	14,07	14,04
	4,720	2,03	14,13	
2-Mercaptobenzthiazole (Captax) 	2,540	3,04	38,22	38,34
	2,020	2,41	38,26	
p-Thiocyanatochlorobenzene $p-ClC_6H_4SCN$	2,920	1,71	18,78	18,88
	3,750	2,18	18,64	
Sodium β-sulfopropiononitrile	4,510	2,85	20,26	20,36
	3,930	2,50	20,40	
2,5-Anhydro-1-chloro-3-methoxy-4-tozylxylite	5,290	2,25	13,64	13,91
$CH_2Cl \cdot CH \cdot CH(OCH_3) \cdot CH(O_3SC_7H_7) \cdot CH_2$	5,330	2,26	13,91	
Sodium bromoethanesulfonate $BrCH_2 \cdot CH_2SO_3Na$	5,050	2,35	14,93	15,19
	3,770	1,74	14,81	
Ditozylmonochlorohydrin mixture	4,870	2,08	13,70	13,91
Xylethane C	5,380	2,31	13,77	
p-Dibromobenzene	~3,500			

A mixture of 10 ml of twice distilled water, 1 ml of 0.5 N NaOH, and 2-3 drops of 30% hydrogen peroxide was used as the absorption solution.

After an aliquot of sample had been burnt, and the combustion products had been absorbed for 8-10 min, the flask stopper and the platinum grid were rinsed with 50 ml of twice distilled water. The contents of the flask were evaporated to the damp salt state in the presence of a small amount (about 200 mg in two parallel samples) of platinum black [14] to remove excess peroxide. Five ml of water and 5 ml of dilute (2 : 3) acetic acid were added to the flask, and the mixture boiled for one minute (no longer) to remove CO_2. Ten ml of ethanol and three drops of a 0.1% aqueous solution of sodium alizarinsulfonate were added to the cooled solution, which thereby acquired a yellow color. When the solution had a rose or a distinctly rose tinge after addition of the alcohol, then a further small amount of acetic acid (0.5-1 ml) was added until the color changed to yellow. The contents of the flask were titrated with 0.03 N $Ba(NO_3)_2$ until the color changed to rose. Just before the end point, titration was carried out slowly, and the color of the solution being titrated was compared with the color of a sample whose determination had been carried out in parallel. Two drops of reagents were sufficient to change the color.

The amount of sample taken is altered in accordance with the percentage sulfur content of the test compound. For compounds containing 10-20%, 20-30%, and 30-40%, sample weights of 4-5, 3-3.5, and 2-2.5 mg are recommended.

When the sulfur content is very low the sample weight can be increased to 8-10 mg.

TABLE 2

Determination of Sulfur in Polymeric Compounds*

Sample No.	S content, % by combustion in a flask	S content, % by hydrogenation**	Sample No.	S content, % by combustion in a flask	S content, % by hydrogenation**
1	8,02 7,81	7,73	5	6,04 5,79	5,57
2	9,19 9,12	9,19	6	5,32 5,42	5,29
3	7,26 7,30	7,23	7	5,54 5,50	5,49
4	8,85 8,62	8,86			

* The polymeric compounds contained sulfur, chlorine, and nitrogen in addition to carbon, hydrogen, and oxygen; sample No. 6 also contained sodium

** E. S. Pisarenko carried out the hydrogenation method of analysis.

The $Ba(NO_3)_2$ solution was standardized against chemically pure grade K_2SO_4 (heated to constant weight at 105°) by a method similar to that mentioned above (without any addition of peroxide and platinum black); 1 ml of 0.02 N $Ba(NO_3)_2$ = 0.32066 mg S.

SUMMARY

A technique for the rapid microdetermination of sulfur in organic monomeric and polymeric compounds is described. Sulfur (2-40%) can be determined (with an accuracy of ± 0.3%) in materials containing chlorine, bromine, nitrogen, and the alkali metals.

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A GENERAL METHOD FOR THE QUANTITATIVE DETERMINATION OF THE ANHYDRIDES AND CHLOROANHYDRIDES OF CARBOXYLIC ACIDS

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It was shown in 1956 [1] that the reaction of anhydrides and chloroanhydrides of carboxylic acids with aromatic amines is a very promising basis for the determination of these anhydrides, excess of amine being titrated potentiometrically by a diazometric method [2]. The suggested method has, however, only proved to be effective in the case of halogenoanhydrides. With the anhydrides, this method has proved to be suitable only for the most reactive ones (acetic and maleic anhydrides). Thus, in order to get complete reaction in the case of benzoic anhydride, it was necessary to heat it with an aromatic amine in a nitrobenzene solution at 150° for two hours, while such compounds as phthalic and succinic anhydrides could not be quantitatively converted into their amides even after several hours heating.

Recently we were able to show that carboxylic acids, on addition to an inert solvent, very strongly catalyze the reaction of an aromatic amine with anhydrides and chloroanhydrides [3-5]. Depending on the nature of the acid added and its concentration, it has been shown that the rate of acylation can be increased a few thousand times; it was also demonstrated that anhydrides which are normally inert in such reactions are particularly susceptible to this catalytic action. The discovery of this effect has made it possible to develop a more general and universal method for the determination of anhydrides and halogenoanhydrides of carboxylic acids, than the one we suggested earlier [1] (compare [6]).

EXPERIMENTAL

More than 20 aromatic and aliphatic anhydrides and chloroanhydrides were tested; equally good results were obtained. The most typical examples are given in the table.

Each of the test materials was subjected to a purification which ensured almost 100% pure products. By dissolving accurately weighed aliquots of these materials, 0.2 M solutions in an organic solvent were prepared; 0.2 ml lots of this solution were used for analysis.

Meta-chloroaniline was chosen as the amine, since it had the advantages over other amines, of giving better results during its titration, and of being readily acylated in mixtures of inert solvents and acetic acid. Samples of this amine which had been carefully purified for kinetic research [4], as well as samples obtained by a double distillation, proved to be equally suitable.

It was established that determinations can be carried out equally readily in benzene and nitrobenzene (both chemically pure grade solvents which had been dried and redistilled beforehand); nitrobenzene, however had the decisive advantage of being an outstanding solvent.

Test material	Sample wt., mg	Medium	Heating time, min	Mean value from several determinations
Acetic anhydride	4,08	NB + HAc	3	99,2±0,4
» »	4,08	B + HAc	5	99,1±0,3
Benzoic anhydride	9,07	NB + HAc	5	100,0±0,3
» »	9,07	B + HAc	10	100,3±0,1
Maleic anhydride	3,92	NB + HAc	3	100,2±0,4
Phthalic anhydride	5,91	NB + HAc	30	100,0±0,8
Succinic anhydride	3,99	NB + HAc	60	100,4±0,4
Acetyl chloride	3,14	NB + HAc	3	99,6±0,4
Benzoyl chloride	5,62	NB + HAc	3	99,6±0,5
»	5,62	B + HAc	5	99,5±0,6
p-Nitrobenzoyl chloride	7,42	NB + HAc	3	100,2±0,5

Note: B = benzene; HAc = acetic acid; NB = nitrobenzene

Initially we carefully purified and dehydrated the acetic acid as recommended in a previous article [7]; we subsequently established that chemically pure grade glacial acetic acid could be used without further purification. It should, however, be emphasized that some commercial glacial acetic acid contains traces of acetic anhydride as an impurity and this can lead to incorrect results. It is therefore essential to check, as indicated below, on the stability of solutions of m-chloroaniline in the acetic acid–inert solvent mixture.

Before carrying out any determinations, it is essential to carry out control tests to ensure that the solutions and the solvents used are free from materials which can react with sodium nitrite in an acid medium.

Solution of m-Chloroaniline in an Inert Solvent. In 100 ml of benzene or nitrobenzene, 0.35 g of the amine is dissolved; the solution is stored in a ground glass stoppered flask. The amine concentration remains unchanged for at least a month.

Determination of Sodium Nitrite Solution : m-Chloroaniline Ratio. Exactly 0.4 ml of a 0.2 M solution of m-chloroaniline in benzene or nitrobenzene was transferred to a 100 ml beaker; 10 ml of glacial acetic acid, 1 ml of 8% hydrochloric acid, and 0.5 g of solid potassium bromide were then added; the mixture was diluted to a volume suitable for titration (40-50 ml) and the amine titrated at room temperature with 0.01 M sodium nitrite solution from a 10 ml microburet having scale divisions of 0.02 ml, as in the method published earlier [2]. The emf was measured after the stirrer was switched off and the layers had separated. Care was taken to ensure that the platinum electrode was completely immersed in the aqueous layer. The mean value obtained from several such determinations was used for all subsequent determinations.

Testing for Absence of Acetic Anhydride in Acetic Acid. A mixture of 0.4 ml of a 0.2 M solution of m-chloroaniline in benzene or nitrobenzene and 0.4 ml of glacial acetic acid was kept at 70° for two hours; in the absence of anhydride, the amount of amine taken remained constant. It decreased significantly only on heating the mixture for four hours at 90-95°. When such a long period of heating is necessary in the course of a particular determination, control tests must be carried out.

Acylation. 0.4 ml of glacial acetic acid and 0.6 ml of 0.2 M m-chloroaniline in benzene or nitrobenzene were introduced into a test tube (100 ml long and 10 mm diameter): an aliquot (0.04 mM) of the test anhydride or chloroanhydride was then added. The mixture was thoroughly mixed, the test tube was connected to an air condenser and placed on a water bath at 65-70°. Depending on the anhydride taken, the heating time varied from three minutes to one hour. After being cooled, the contents of the test tube were rinsed with several portions (a total of 10-15 ml) of glacial acetic acid into a titration beaker, and the excess m-chloroaniline titrated as indicated above.

The anhydride content was calculated by means of the following formula:

$$P = \frac{M \alpha N \cdot 100 (v_1 - v_2)}{A},$$

where M is the molecular weight of the anhydride or chloroanhydride, A is the sample weight (mg), N is the

normality of the nitrite solution, α is the correction factor for the normality, v_1 and v_2 the volumes of nitrite (ml) used for titrating the amount of m-nitroaniline taken for the acylation and for titrating excess of the amine.

Results for determination of anhydrides and chloroanhydrides are given in the table.

Statistical treatment of the results obtained [8] showed that the accuracy of the values obtained is not less than 1%.

For macrodeterminations, 0.05-0.1 M sodium nitrite and a 50 ml buret should be used, while the amount of test material, m-chloroaniline, solvent, and catalyst should be correspondingly in eased.

SUMMARY

A general method has been developed for the quantitative determination of anhydrides and chloroanhydrides; it consists in treating the test material with excess m-chloroaniline in a mixture of an inert solvent and acetic acid (the catalyst), with subsequent back potentiometric titration of the residual amine with sodium nitrite. The method permits a rapid and fairly accurate (up to 1%) determination of both micro- and macroamounts of anhydrides and chloroanhydrides of carboxylic acids.

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DETERMINATION OF MONOHYDRIC PHENOLS BY PARTITION CHROMATOGRAPHY AND ULTRAVIOLET SPECTROPHOTOMETRY

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The present article is devoted to a study of the possibility of analyzing four component mixtures containing phenol and the isomeric cresols by partition chromatography (for separating the phenol mixtures) and ultraviolet spectrophotometry.

The method developed has been applied to the determination of phenols in drainage water from peat gas-generator stations and in the raw material used for plastics production. The mobile solvent used for chromatographic separation was isooctane, while the staionary phase was water.

Similar work already carried out was either with a different solvent, e. g., cyclohexane [1, 2] or with different phenols, when isooctane was used [3].

The discrepancies between published absorption coefficients [4, 5, 6] necessitated a fresh determination. Thus, in the case of p-cresol at $\lambda = 285.8$ mμ these discrepancies amount to about 12%, while for phenol at $\lambda = 271$ mμ, the discrepancies amount to 30-40%. For o- and p-cresols, they are not high.

Measurements were carried out on a SF-4 spectrophotometer in the spectral region 240-300 mμ, using quartz cuvettes with a layer thickness of 1 cm. Corrections for contamination of the cuvette were applied in all the determinations. Measurements were carried out at each wave length for the smallest slit width for which the sensitivity of the apparatus according to the potentiometer was still zero. The slit width was varied from 1.1 to 0.3 mm.

The absorption coefficients were determined for concentrations of 0.04-0.063 g/liter. During chromatographic separation, the concentration of the materials in the eluate lay mainly in the range 0.02-0.06 g/liter. At these concentrations, solutions of phenol and cresols in isooctane conform to Beer's law [5].

The optical purity of the isooctane (over the working range) was ensured by purifying the commercial product chromatographically.

The starting materials, which were contaminated by oxidation products, were purified by distilling them twice, and recrystallizing them once from optically pure petroleum ether. The exception was m-cresol, which was not recrystallized, and was accordingly not pure enough (b. p. 197°). Different melting points have been ascribed to phenol, o- and p-cresols, by different authors. The temperatures which we determined for our products agreed with the results given in [6-9]; they were 40.9° for phenol, and 30.9° and 34.9° for o- and p-cresols respectively.

In order to exclude errors as much as possible, both during weighing of the original materials, and during spectroscopic measurements (cleanliness of the curvette, setting the slit width and the wave length), 5-6 determinations of the absorption coefficient were carried out for each material. Freshly prepared solutions were used in each case, while the materials used for making up the solutions were recrystallized beforehand.

TABLE 1

Absorption Coefficients of Phenol, m-, and o-Cresols

Wave length	m-Cresol				o-Cresol				p-Cresol				Phenol		
	[4]	[5]	[6]	our results	[4]	[5]	[6]	our results	[4]	[5]	[6]	our results	[4]	[5]	our results
270	12,92	13,10	—	12,32	16,09	16,13	—	15,85	13,37	12,10	—	12,49	23,93	18,47	18,27
271	14,23	15,55	—	13,09	17,10	16,10	—	16,92	12,19	11,48	—	12,49	25,89	18,47	20,71
272	15,82	15,70	—	13,95	17,30	16,15	—	17,15	13,01	12,55	—	12,89	18,90	14,56	17,29
272,8	15,82	15,65	15,70	14,24	16,40	16,29	16,41	16,53	14,77	13,62	14,68	13,84	14,20	11,32	13,29
275	12,08	11,10	—	11,71	12,50	12,29	—	12,96	14,89	13,70	—	14,74	10,77	9,03	9,19
277,4	10,50	10,50	10,28	10,00	15,84	15,65	15,89	15,28	15,65	15,52	15,33	16,06	25,40	17,62	18,36
278	12,49	12,30	—	—	16,34	15,87	—	15,94	16,69	16,67	—	16,48	21,52	12,87	17,58
279	16,87	16,0	—	14,22	14,32	15,22	—	14,69	20,48	18,43	—	18,75	12,28	7,68	11,40
185,8	0,90	0,98	0,00	0,83	0,70	0,22	0,73	0,65	18,78	17,15	19,30	17,42	—	—	0,25

The mean arithmetic values of the absorption coefficients obtained are given in Table 1. With the exception of m-cresol, the values mainly lay between the published values [4-6].

When the mean values of the absorption coefficients were used in calculations during chromatographic separation of synthetic mixtures, a good balance among the materials was obtained.

Absorption curves of phenol and the cresols are shown in Fig. 1.

Table 2 contains the absorption maxima of the same materials. The biggest difference in the positions of the maxima according to our results and published data [4, 5] amounted to 0,8 mμ.

Silica gel prepared by Ramsey and Patterson's method [10] was the sorbent used. It should be pointed out, however, that silica gel prepared according to this method does not always prove suitable for use because of the formation of a large amount of fine particles, which are not removed on sieving through a 200 mesh sieve. The fine particles were removed by suspending the silica gel in water and siphoning off the upper layer. Ten minutes were allowed to elapse between making a suspension and siphoning off the upper layer [11]. The silica gel was dried at 100-105° for 24 hours. The silica gel fraction passing through a 100 mesh sieve but retained on a 200 mesh sieve was used for partitioning (American standard). After use the silica gel was regenerated by washing with distilled water.

The apparatus used (Fig. 2) for partition chromatography was similar in the main to that use by Sweeney and Bultman [3]. It consists of a column 18 mm in diameter and 300 mm long. It is possible to carry out partitioning under pressure in this apparatus. Nitrogen supplied from a cylinder supplied the pressure.

Before use, water and isooctane were mutually saturated with each other. Water was added to 19 g of silica gel in the maximum possible amount which still left the silica gel in the form of a dry powder (it does not cling to the walls and does not gelatinize in the isooctane). Taking into account the original moisture content of the silica gel, the amount of water added was slightly greater than 90% by weight of the dry silica gel. One hundred ml of isooctane was then poured onto the silica gel; it was carefully freed from air bubbles and transferred to the column. When air bubbles appeared in the column they were removed by means of a glass rod. The sorbent was packed to give a column with a constant height by rotating the column in one direction. The silica gel column was finally packed by applying a pressure of 150 mm Hg. During packing, the sorbent took up 50-60 ml of isooctane. The height of the sorbent amounted to 180-195 mm.

TABLE 2

Absorption Maxima of Phenol and Cresols

	$\lambda_{max.}$, mμ			
	o-cresol	m-cresol	p-cresol	phenol
Our results	271,8; 278	272,6; 279,6	270,4; 273,4; 276,4; 279,2; 285,75	264,6; 270,8; 277,8
[4]	271,6; 277,8	272,4; 279,4	270; 273; 276; 279; 285,6	264,4; 270,8; 277,4
[5]	271; 278	272; 279	270; 272,8 276; 279; 285	265; 270; 277,4

It should be pointed out that in similar papers [1, 2], separation of phenolic mixtures was carried out using a column of sorbent with a different height although the diameter of the column was the same, i. e., 18 mm. When cyclohexane was used as the mobile solvent, separation of phenol and cresols occured on a silica gel column with a height of 500 mm (56 g). On a silica gel column with a height of 150 mm (19 g) only phenol is separated from the cresols. In our experiments, separation of the four component mixture of phenols occurred on a sorbent with a height of 500 mm; the weight of silica gel was 19 g, and this was sufficient to give the indicated height of packing. This, presumably, is determined by the partition coefficients of the test materials in the different solvent systems: cyclohexane–water and isooctane–water.

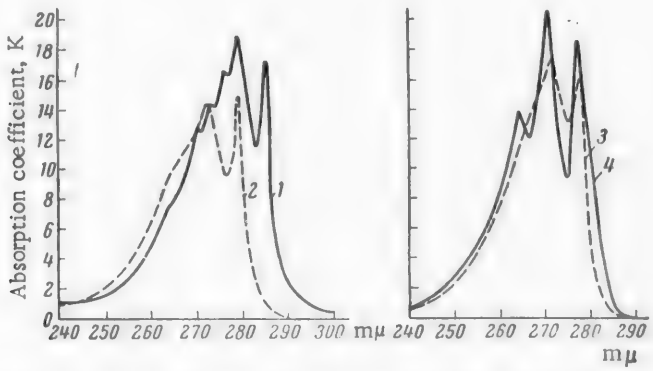

Fig. 1. Absorption curves in isooctane: 1) p-Cresol; 2) m-cresol; 3) o-cresol; 4) phenol.

A synthetic mixture of the following composition was used for partition chromatography: 0.451 g phenol/liter, 0.431 g o-cresol/liter, 0.414 g p-cresol/liter, and 0.359 g m-cresol/liter. The same materials as those used for determination of the absorption coefficients were used for preparing the synthetic mixtures. When the column had been prepared as indicated above, and the level of the solvent had reached the surface of the sorbent, but had not yet passed through it, 5 ml of a synthetic mixture was introduced into the column. The column walls were rinsed with a small amount of isooctane (2 ml) after the test sample had almost completely passed into the sorbent but the surface of the latter had not been exposed. This operation was repeated. The solvent flow and the pressure were then controlled so that the rate at which the eluate issued from the column was 2 ml/min. The eluate was collected in calibrated test tubes in 5 ml portions, from the moment at which the test sample was introduced into the column.

TABLE 3

o-Cresol			m-Cresol			p-Cresol			Phenol		
introd. into col., %	calc. value, %	Δ, %	introd. into col., %	calc. value, %	Δ, %	introd. into col., %	calc. value, %	Δ, %	introd. into col., %	calc. value, %	Δ, %
26,1	26,3 26,1	+0,2 0,0	21,3	21,6 22,1	−0,2 +0,3	25,0	23,3 23,6	−1,7 −1,4	27,2	28,9 28,3	+1,7 +0,9

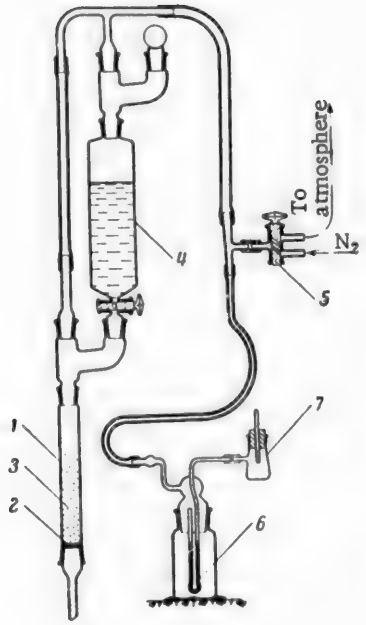

Fig. 2. Chromatographic apparatus. 1) Column; 2) sintered glass disc; 3) sorbent; 4) solvent container; 5) two-way tap; 6) manometer; 7) mercury trap.

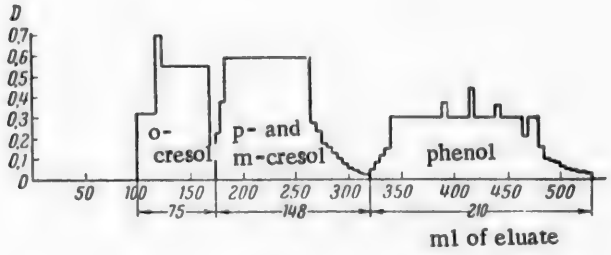

Fig. 3. Chromatogram of a synthetic mixtures of phenols.

When the flow rate is uneven and pulsating, clearly defined boundaries between the issuing materials are not obtained. When the elution rate is uniform, not less than 110 test tubes should be collected (550 ml approximately).

The contents of the test tubes were then examined spectrophotometrically. In order to speed up the spectrophotometric measurements the elution limits of the individual materials were determined.

On passing through the column the mixture of four phenols separates into three fractions with characteristic absorption curves. A chromatogram obtained during one of these experiments is shown in Fig. 3. In this figure, the maximum optical density of the eluate is plotted along the ordinate, i. e., the optical densities of the chromatographic fractions with the highest maxima on the absorption curve, while the amount of eluate (in ml) is plotted on the abscissa. In Fig. 3 the horizontal parts correspond to combined portions of the eluate, while the peaks correspond to the points at which the elution boundaries of the fractions were determined.

The concentration of the issuing component, and, accordingly, its optical density, increases from the point at which it appears in a given fraction; it then reaches a maximum and then falls right down to zero towards the end of elution (the family of curves in Figs. 4-6).

The order in which the fractions come through the column is o-cresol first (Fig. 4), this is followed by m- and p-cresol together (Fig. 5), and finally phenol (Fig. 6).

Before the appearance of o-cresol, pure solvent issues from the column, and this has an optical density of approximately 0.03 (at $\lambda = 270$ mμ). It was established experimentally that only 100 ml of pure solvent comes through, 65-110 ml with o-cresol comes next, followed by 150-175 ml with the mixture of p- and m-cresols, and approximately 200 ml with phenol.

The amount of o-cresol and phenol issuing separately was calculated by means of the formula:

$$g = \frac{D \cdot V}{K \cdot l} \qquad (1)$$

where g is the amount of test material (g), D is the optical density, V is the volume of fraction being analyzed, K is the absorption coefficient (ml/cm), and l is the thickness of the absorbing layer (cm).

When such solvents as cyclohexane–water and isooctane–water are used, separation of m- and p-cresols to the individual compounds does not occur because of the small differences in the partition coefficients. Accordingly, the concentration of m- and p-cresols in the eluate was determined by solving the system of equations:

$$\begin{aligned} D_{\lambda_1} &= K^{(1)}_{\lambda_1} x_1 + K^{(2)}_{\lambda_1} x_2 \\ D_{\lambda_2} &= K^{(1)}_{\lambda_2} x_1 + K^{(2)}_{\lambda_2} x_2 \end{aligned} \qquad (2)$$

In equations (2) x_1 and x_2 are the corresponding concentrations in g/ml.

It was established that results which showed the best agreement in the case of phenol and o-cresol are obtained at wave lengths corresponding to the widest absorption maxima of these compounds, namely: λ = 271.8 mμ and K_λ = 17151 for o-cresol, and λ = 270.8 mμ and K_λ = 20826 for phenol. In the case of m- and p-cresols, the best results were obtained at wave lengths corresponding to the following maximum for the combined absorption curve: λ_1 = 273 mμ and λ_2 = 285.75 mμ. For the wave lengths indicated the absorption coefficients are: K_{λ_1} = 14.170 and K_{λ_2} = 833 for m-cresol, and K_{λ_1} = 14.052 and K_{λ_2} 17.425 for p-cresol. The ratio of the absorptions of these two compounds is a maximum at the chosen wave lengths.

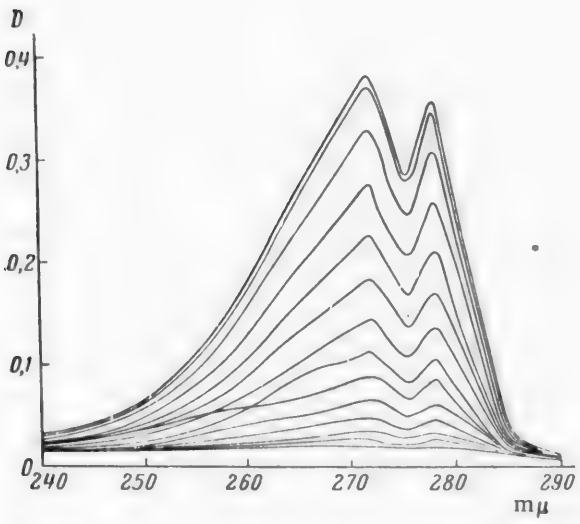

Fig. 4. Absorption curve of the first chromatographic fraction.

Results for two quantitative determinations of a test mixture are given in Table 3; these results show that a separation efficiency of not less than 0.5% is possible for o- and m-cresols, while for phenol and p-cresol this efficiency is 2%.

The low absorption coefficients obtained for m-cresol, as compared with published results, reflect on the accuracy with which p-cresol is determined. The accuracy with which p-cresol and phenol can be determined could be increased by determining the absorption coefficients of m-cresol and phenol more accurately.

The method discussed has been used for establishing the presence of phenol and cresols in the residue from drainage water from peat gas-generator stations working on lowland peat. The residue is obtained by evaporating 85% of the acidified drainage water during purification, and could serve as a rich source of valuable chemicals, e. g., phenols. The lack of information on the chemical composition of the phenols in this drainage water from peat gas-generator stations, and lack of information on the residue, makes it difficult to choose the best way of using it. The residue was extracted with benzene and butyl acetate. Fatty acids were removed by treating the extracts with sodium carbonate solution. The phenols were isolated as phenates by treating the extracts with sodium hydroxide solution. The phenate solution was acidified, and the phenols extracted with ethyl ether; after evaporating off the ether and drying the residue over sodium sulfate, the residue was distilled under a vacuum of 5 mm Hg. Phenol and cresols were determined in the distillate, the temperature range of which reduced to 760 mm Hg was 180-230°. Thirty-two liters of the original water was required in order to obtain 10 g of phenols

TABLE 4

p-Cresol		Phenol	
in separate determinations, %	mean, %	in separate determinations, %	mean, %
3,0 2,8	2,9	33,8 34,3	34,0

TABLE 5

Phenol, %	p-Cresol, %	m-Cresol, %	Unknown, %
6,8	26,2	48,8	18,2
18,0	18,8	30,5	32,7
12,9	23,3	42,2	21,6

from the distillate, since the phenols content of the drainage water from the peat gas generating stations amounted to 5-7 g/liter of volatiles and 2-3 g/liter of nonvolatiles. When a test sample was analyzed by partition chromatography, three fractions were obtained as in the case of experiments with the synthetic mixture. The absorption curves of the first fraction, however, did not coincide with the curves for pure o-cresol. The absorption maxima of the subsequent fractions and of pure p-cresol proved to be the same and were found to be: 270.6-270.8; 273.0-273.4; 276.2-276.4; 279.4; 285.75 mμ.

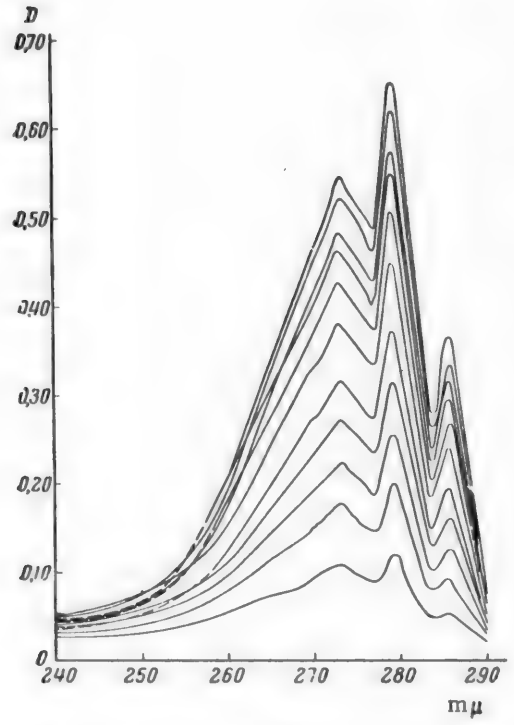

Fig. 5. Absorption curve of the second chromatographic fraction.

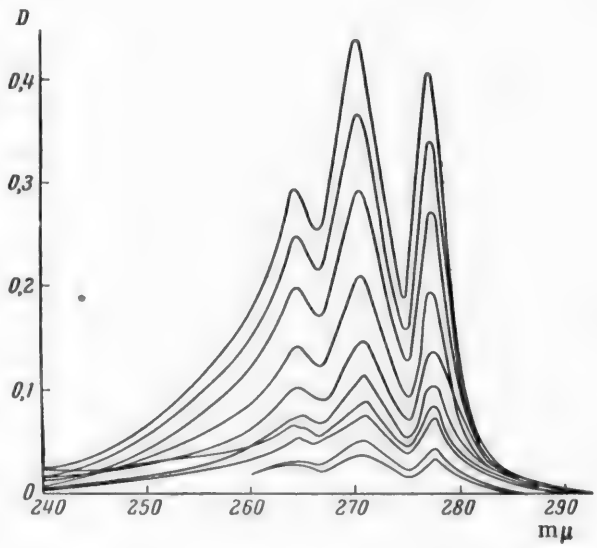

Fig. 6. Absorption curve of the third chromatographic fraction.

A comparison of the absorption curves of the given fraction with the curves for pure p-cresol shown in Fig. 7 shows that they are similar in shape. The test fraction therefore contains p-cresol.

The next fraction contains phenol, since the absorption curves of this fraction and of phenol are identical. Results of two parallel analyses of the test distillate obtained from the residue are given in Table 4. The deviation in the two parallel determinations amounts to 0.5% for phenol, and 0.2% for p-cresol. The phenol and p-cresol contents of the original water are therefore 0.0111 and 0.0095 g/liter · respectively.

During the analysis of so-called tricresols (raw material used for plastics production), we determined phenol, m- and p-cresols. The raw material was obtained from the "Plastmass" factory in Sverdlovsk where control of

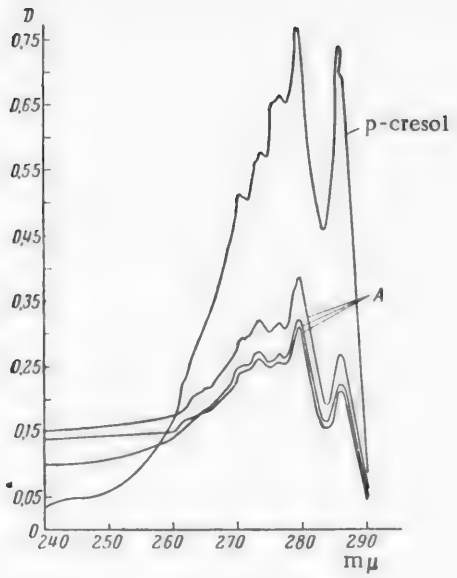

Fig. 7. Absorption curves of pure p-cresol and of the second chromatographic fraction of phenols from the residue with a boiling range of 180-230°.

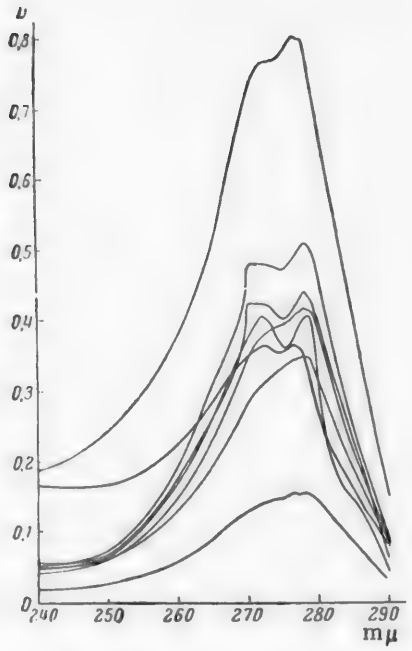

Fig. 8. Absorption curve of the chromatographic fraction issuing from the column before p- and m-cresols.

raw material is not carried out since no suitable analytical methods are available there. Results of the analysis of three samples are given in Table 5. The absorption curves of the fractions preceding the p- and m-cresols fractions are shown in Fig. 8; these curves indicate that the given fraction cannot be o-cresol. In this instance, as in the case of the residue mentioned above, other phenols presumably interfere with the determination of o-cresol. Pearson [2] has shown that during the separation of a thirteen component mixture of phenols consisting of phenol, cresols, xylenols, and ethyl phenols, o-cresol issues from the column with 2,4-xylenol, while the ethyl phenols and the remaining xylenols are eluted earlier.

SUMMARY

A method has been developed for the determination of phenol, o-, p-, and m-cresols in each others presence the method is based on partition chromatography and ultraviolet spectrophotometry; isooctane is used as the mobile phase while water is used as the stationary phase. The experimental accuracy is not less than 2%.

Other phenol homologs interfere with determination of o-cresol.

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BRIEF COMMUNICATIONS

DIRECT FLUOROMETRIC DETERMINATION OF ALUMINUM BY MEANS OF HEMATOXYLIN

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Kazan Aviation Institute
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At present there are still very few suitable and faultless methods for the volumetric determination of aluminum. According to Kolthoff [1], during titration of aluminum sulfate with alkali using phenolphthalein as indicator, the end point occurs before the equivalence point; when aluminum chloride is determined under the same conditions, the amount of alkali used corresponds to the theoretical value. Direct complexometric titration is unsuccessful even when alizarin S, stilbazo, chromazurol S, and other indicators are used. Since titration can only be carried out at pH 4.0 when these indicators are used, some of the aluminum is not complexed by sodium ethylenediaminetetracetate (EDTA-Na) [2]. Back titration of excess EDTA-Na with a standard $ZnSO_4$ solution with eriochrome black T, or with a $FeCl_3$ solution using salicylic acid [3], also possesses some drawbacks.

Our experiments have shown that the fluorometric method described by Tanaev [4] is worthy of attention. The method is based on formation of a sparingly soluble complex of the cryolite type $Na_3[AlF_6]$; trivalent iron and chromium ions form similar compounds.

During direct titration, a standard solution of the fluoride of an alkali metal is added to the test aluminum solution until some effect corresponding to an end point is observed. Excess fluoride could also be back titrated with a standard solution of an aluminum salt. Since an aqueous solution of an alkali metal fluoride has an alkaline reaction (pH 8.0), while that of an aluminum salt is acid (pH 3.5), when all the fluoride has been complexed, the excess of aluminum salt gives the solution an acid reaction which is detectable by the color change of methyl red or phenol red. Titration is carried out in the presence of NaCl in order to depress the solubility of the precipitate. Under these conditions, formation of $Na_3[AlF_6]$ proceeds even at pH 7.3-7.4 without simultaneous precipitation of $Al(OH)_3$. The method gives good results as long as certain conditions are observed; the main condition is the absence of free acids or alkalis in all the solutions; they will naturally distort the results, since titration is carried out with acid–base indicators.

The original materials used for preparing the working solutions must be purified most carefully when fluorometric titration is used. Aluminum preparations, even highly pure grade materials, may either contain free acid or basic salts; the latter liberate free alkali when they enter into reaction with fluoride ($Al[OH]^{2+} + 6F^- = [AlF_6]^{3-} + OH^-$). Alkali metal fluorides often contain Na_2SiF_6, Na_2SiO_3, Na_2CO_3, as impurities, these also form alkalis on hydrolysis. This means that during titration, the indicator acquires an intermediate color which interferes with exact establishment of the end point.

We set ourselves the problem of developing a method for the direct titration of Al^{3+} ions in which the end point is established, not by changes in the color of methyl red or phenol red, but by means of hematoxylin. The latter, although it belongs to the group of acid–base indicators for which the limits of the color change from yellow to violet are pH 5.0-6.0, does, in addition, possess the capacity of forming colored compounds with the ions of many metals. These compounds are regarded at present as inner complex compounds [5]. Such compounds, in most cases, are unstable in the presence of free acetic acid; under these conditions the color of the aluminum lac does not change.

TABLE 1

Aluminum taken, mg	Volume of KF solution (ml) and its normality	Aluminum found, mg	Difference, mg	Error, %
13,53	5,90 (0,499)	13,25	—0,28	2,0
12,04	5,25 (0,499)	11,79	—0,25	2,0
6,67	9,00 (0,1665)	6,74	+0,07	1,1
7,05	9,25 (0,1665)	6,98	—0,07	1,0
5,95	8,07 (0,1665)	6,04	+0,09	1,5
2,71	3,57 (0,1665)	2,67	—0,04	1,5
1,85	2,57 (0,1665)	1,88	+0,03	1,5
4,49	4,00 (0,2495)	4,49	0	
1,80	1,60 (0,2495)	1,80	0	
1,80	1,62 (0,2495)	1,82	+0,02	1,1

TABLE 2

Test material	Sample wt. mg	Amount of aluminum, mg	Volume of 0.128 N KF solution (ml)	Aluminum found, mg
Aluminum	10,06	9,97	17,32	9,97
Ditto	10,06	9,97	17,34	9,98
» »	10,06	9,97	17,35	9,99
Magnesium MLZ	50,7	0,98	1,70	0,99
Ditto	50,7	0,98	1,72	1,00
» »	50,7	0,98	1,73	1,01

Wildenstein [6] introduced hematoxylin $C_{16}H_{14}O_6 \cdot 3H_2O$ into analytical practice for the qualitative detection of the cations of certain metals (copper, lead, tin, antimony, etc.). Hematoxylin later found applications in photometric methods of analysis, although the literature published on these applications is small. Thus Hatfield [7] developed a method for controlling the content of aluminum compounds in water after purification of the latter. Tartakovskii [8] successfully used hematoxylin for the photometric determination of aluminum, tin, molybdenum, and chromium. Cherkesov and Busev [9] have recommended hematoxylin for spot test detection of antimony. Ch'ien Ts'ui Lin [10] introduced hematoxylin into complexometry for the indirect determination of aluminum.

The aluminum lac has a lilac or red-violet tinge which is preserved at pH 4,5-8,5; the composition of the compound varies with the analytical conditions, but this has no effect on the accuracy of the modified method which we have developed for the fluorometric titration of aluminum. According to Tartakovskii, the interaction of aluminum with hematoxylin proceeds as follows:

$$3C_{16}H_{14}O_6 + Al(OH)_3 = Al(C_{16}H_{13}O_6)_3 + 3H_2O.$$

We noticed that when an alkali metal fluoride is added to this compound in an acetic acid medium at pH 4,6-5,2, the compound is readily destroyed by fluoride ions, and the violet color of the lac disappears. The liberated hematoxylin colors the solution yellow, the latter being the characteristic color of the indicator itself in an acid medium. This process occurs at ordinary temperatures, but better at 50-60°.

Denoting the violet complex of aluminum with the dye by MeR the general scheme of the reaction can be written thus:

$$\underset{\text{(Violet)}}{MeR} + F^- \rightleftarrows \underset{\text{(Colorless)}}{MeF} + R^-$$

TABLE 3

Al content of the solution, mg	Volume of 0.128 N KF, ml	Al found	
		mg	%
4,45	7,68	4,42	99,4
4,45	7,70	4,43	99,5
6,25	10,90	6,27	100,4
6,25	10,88	6,26	100,2
6,25	10,85	6,25	100,0

Babko [11] has shown that the ratio $[MeF] : [F^-] = K_{MeR} : K_{MeF}$ characterizes the extent to which the fluoride ions is complexed; it will be a maximum under conditions such that $K_{MeR} >> K_{MeF}$, i. e., when the stability of the colored compound MeR is considerably less than that of the fluoride compound MeF of the same metal. Since the instability constant of the $[AlF_6]^{3-}$ is very small and is equal to 1.44×10^{-20}, the equilibrium of the reaction shown above can be regarded as being shifted almost completely to the right hand side.

This reaction was made the basis of a direct, and when necessary, a back fluorometric titration of aluminum in acetic acid medium using hematoxylin as indicator.

Standard solutions of potassium fluoride and aluminum sulfate whose ratio to each other is known are required. Hematoxylin is used as a 1% alcohol solution.

Technique. To a measured volume of a solution of an aluminum salt containing 2-10 mg of the latter, is added 1 ml of 30-40% acetic acid, and the volume made up to 25 ml with water. The solution is heated to 50-60° and sodium chloride added until the solution is saturated with it, 1-2 g of crystalline $NaC_2H_3O_2 \cdot 3H_2O$ is added and aluminum ions titrated with 0.2 N KF in the presence of hematoxylin until the violet color of the solution changes to a pure yellow which is the color of the acid form of the indicator.

To avoid precipitation of basic salts, sodium acetate should be added several times during titration in small portions, so that the acidity of the solution slowly drops to the requisite pH value as the end point is approached.

Toward the end of the titration the solution temperature should be kept at 50-60°.

If a back titration technique is adopted, a standard solution of aluminum sulfate (alum) is used, and titration is carried out from yellow to violet. The color change of the hematoxylin is sharp and reversible for forward and back titration.

It is only when the solution being titrated is allowed to stand for a long time that the color pales as a result of adsorption of the dye by the precipitated cryolite.

The color weakens and even completely disappears in solutions whose pH is below 4.5.

Experiments were carried out with solutions of chemically pure aluminum ammonium alums which had been standardized gravimetrically as Al_2O_3; in experiments Nos. 3, 4, 5, and 6 the solutions also contained magnesium, zinc, and manganese sulfates in the proportion of Al : Mg = 1 : 50 and Al : Zn (Mn) = 1 : 10.

Separate experiments showed that large amounts of iron, copper, tartrates, citrates, and oxalates in solution interfere with aluminum determination. In particular, as a result of formation of an iron lac, the color of the solution being titrated acquires a dirty tinge.

Results of some determinations are given in Table 1.

The method was also tried on aluminum metal grade Al, containing 99.5% Al and 0.5% Fe, Cu, and Zn and on magnesium metal (electron grade) containing 2% Al. Aliquots of these metals were dissolved in hydrochloric acid (1 : 1), and the aluminum determined on an aliquot of the solution (after adjusting the pH to 4.6-5.2).

Despite the lower solubility of magnesium and calcium fluorides in water (MgF_2 (18°) $-7.6 \cdot 10^{-4}$ g; CaF_2 (18°) $-1.6 \cdot 10^{-4}$ g in 100 g of water) [12] as compared with that of cryolite, when potassium fluoride is added to a solution containing Al^{3+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, and Mn^{2+}, the most stable complex ions $[AlF_6]^{3-}$ are formed first; consequently, aluminum is readily titrated in the presence of the other cations listed (Table 2).

Since the presence of a large amount of foreign salts during formation of colored lacs affects the shade of these lacs, the possibility of omitting sodium chloride was finally examined. Sodium chloride was replaced by ethanol, since Tananaev and Lel'chuk [13] have shown that ethanol supresses the solubility of cryolite in water

appreciably. Thus, while the solubility of cryolite in water is 0.39 g/liter, this material is only soluble to the extent of 0.22 g/liter in 50% ethanol–water.

In our experiments the solutions being titrated contained 30% by volume of alcohol; the results obtained are given in Table 3.

SUMMARY

A method has been developed for the direct and back fluorometric titration of aluminum, using hematoxylin as indicator.

In contrast to the usual fluorometric titration of aluminum, using acid–base indicators in a neutral medium, hematoxylin permits determination to be carried out in an acetic acid medium at pH 4.8-5.0. Large amounts of copper, iron, tartrates, citrates, and oxalates should be absent. The method can be used for the determination of aluminum in the presence of magnesium (1 : 50), calcium, manganese, and zinc (1 : 10).

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GRAVIMETRIC DETERMINATION OF SMALL AMOUNTS OF LEAD BY MEANS OF A SOLUTION OF A DIVALENT CHROMIUM SALT

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Numerous gravimetric, titrimetric, photometric, and other methods exist for the determination of lead [1-9]. Bearing in mind the various disadvantages of current methods of determining this element, we aimed at developing a new method for determining small amounts of lead in various materials by means of divalent chromium salt solution. Divalent chromium salts are very strong reducing agents [10-13]; they reduce arsenic, antimony, copper, tin, silver, and other ions to the elemental state.

Divalent chromium ions quantitatively reduce lead ions to the elemental state in acid media [14]. Our experiments have shown that there are no lead ions present in the filtrate left after filtering off the precipitate. A black precipitate of metallic lead separates out in the cold. The amount of lead is determined gravimetrically. Arsenic and zinc do not interfere with determination of lead by means of a divalent chromium salt. Antimony is partially coprecipitated with lead, but can be separated from the latter.

TABLE 1

Pb taken, mg	Pb found, mg	Pb taken, mg	Pb found, mg
4,0	3,8	2,0	1,8
4,0	4,0	2,0	2,0
4,0	4,0	2,0	2,0
4,0	4,0	2,0	2,0
4,0	4,0	2,0	2,0
4,0	4,0	1,0	1,0

The results given in Table 1 show that separation of lead by reduction with a divalent chromium salt solution gives satisfactory results.

Tables 2, 3, 4, and 5 contain results for the determination of lead in synthetic mixtures containing quinquevalent arsenic, zinc, and quinquevalent antimony. These results show that arsenic and zinc do not interfere with lead determination. Shat'ko [10] has shown that arsenic is precipitated from strongly acid solutions on heating (pH about 0.02). We therefore precipitated lead from solution at pH 3.7. Our experiments confirmed that under these conditions arsenic is not precipitated.

Divalent chromium ions quantitatively reduce quinquevalent antimony to the metallic state from neutral

TABLE 2

(20 mg As^V taken)

Pb taken, mg	Pb found, mg	Pb taken, mg	Pb found, mg
4,0	4,0	2,0	2,0
4,0	4,0	1,0	1,0
2,0	2,0	1,0	1,0

TABLE 3

(20 mg Zn taken)

Pb taken, mg	Pb found, mg
4,0	4,0
4,0	4,0
2,0	2,0
2,0	2,0
1,0	1,0
1,0	1,0

TABLE 4

(20 mg Sb^V taken)

Pb taken, mg	Pb found, mg
4,0	5,6
4,0	5,8
2,0	5,2
2,0	5,4
1,0	4,4
1,0	2,4

TABLE 5

Pb taken, mg	Pb found, mg
4,0	3,8
4,0	4,0
2,0	2,0
2,0	2,0
1,0	1,0
1,0	1,0

or weakly acid solutions [12]. Metallic antimony is oxidized by a standard solution of potassium dichromate in the presence of sulfuric acid (1 : 4). Under the experimental conditions used, antimony is partially precipitated with lead; incorrect results are therefore obtained for lead (Table 4).

To separate lead from antimony, we treated the precipitate on the filter with 0.2 N $K_2Cr_2O_7$ in a mixture with 20 ml of H_2SO_4 (1 : 4). Antimony thereupon dissolves, while the lead remaining on the filter is washed with 96% ethanol and dried at 105° to constant weight. The results obtained are given in Table 5.

Determination of small amounts of lead (about 1 mg/liter) is carried out as follows: the test solution is evaporated on a water bath to a volume of 10-25 ml, the solution is cooled to room temperature and 10-12 ml of 0.5 N $CrCl_2$ solution added, after 5-10 min the metallic lead is filtered off in a Schott No. 4 crucible, washed 2-3 times with 96% alcohol, and dried to constant weight at 105°.

The divalent chromium solution can be prepared by P. P. Shat'ko's electrolytic method [15] or by a modification of N. A. Popov's method [16].

SUMMARY

Divalent chromium ions quantitatively reduce divalent lead to the elemental state at pH 3.7 at room temperature. The precipitated lead is weighed. Quinquevalent arsenic ions and zinc ions do not interfere with lead determination. Under these conditions quinquevalent antimony ions are partially reduced to the elemental state. Antimony is separated from lead by treating the precipitate of the latter with a 0.2 N sulfuric acid solution of potassium dichromate. The gravimetric method gives satisfactory results for lead concentrations down to 1 mg/liter.

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PHOTOMETRIC DETERMINATION OF RHENIUM WITH DIETHYL-DITHIOPHOSPHORIC ACID

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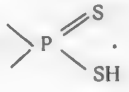
Septivalent rhenium is determined gravimetrically after precipitation by strong organic bases containing N, P, and As. Colored reagents of this type such as methyl violet, methylene blue, rhodamine B, and its esters, have been used for the photometric determination of rhenium. Stannous chloride is the best known and most widely used reagent for rhenium compounds in which the rhenium valence is less than seven, and which are normally prepared by reduction of septivalent rhenium compounds. Almost all the reagents of this group contain N and S in various combinations.

The combination of P and S atoms in a reagent molecule has not yet been examined with respect to rhenium; accordingly, we have examined the interaction of diethyldithiophosphoric acid with rhenium compounds.

This reagent contains the atomic group 

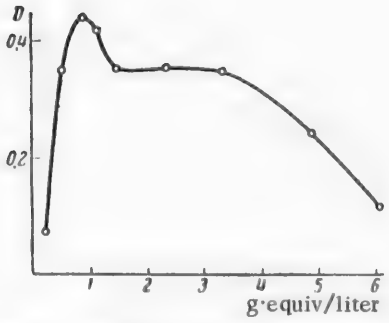


Fig. 1. Relation between the color intensity of the benzene layer and acid concentration.

Diethyldithiophosphoric acid has been used for the detection and determination of molybdenum [1, 2], cadmium, copper, palladium, etc [3]. There is a published reference to the interaction of rhenium with diethyldithiophosphoric acid [3].

Our experiments have shown that in acid media at room temperature, diethyldithiophosphoric acid does not react with septivalent rhenium compounds. When such a solution is heated to boiling, a colored compound is formed. Bearing in mind that diethyldithiophosphoric acid possesses reducing properties [4], we assumed that reduction of the perrhenate ion occurs on heating. We decided that it would be interesting to study this reaction in the presence of a reducing agent, and we chose stannous chloride. Addition of stannous chloride to a mixture of solutions of potassium perrhenate, diethyldithiophosphoric acid, and hydrochloric acid led to the formation of an orange colored compound which was sparingly soluble in aqueous solutions. The compound obtained was soluble in organic solvents.

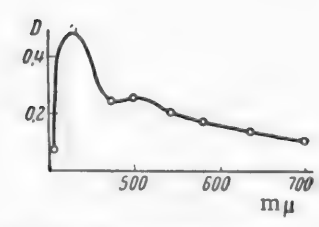


Fig. 2. Absorption curve of a benzene solution.

The reaction conditions were studied photometrically on a FÉK-M photoelectrocolorimeter of the Lang type. Formation of the complex is complete in 10 min; the colored compound can then be extracted with organic solvents.

The complex is stable at hydrochloric acid concentrations of 1-3

TABLE 1

Molar Extinction Coefficients (at 436 mμ)

Solvent	Molar extinction coefficient
Chloroform	$2.8 \cdot 10^2$
Diethyl ether	$4.4 \cdot 10^2$
Ethyl acetate	$5.4 \cdot 10^2$
Benzene	$6.2 \cdot 10^2$
Isobutanol	$6.3 \cdot 10^2$
Isoamyl acetate	$7.7 \cdot 10^2$

TABLE 2

Determination of Rhenium in Pure Solutions

Potassium perrhenate, mg		Mean square deviation, ± %
taken	found	
3,84	3,76; 3,76; 3,80; 3,91; 3,93	1,9
2,56	2,42; 2,48; 2,50; 2,60; 2,64	3,7
1,92	1,80; 1,81; 1,82; 1,92; 1,92	2,7
1,28	1,28; 1,28; 1,28; 1,30; 1,30	0,7
0,64	0,62; 0,63; 0,64; 0,64; 0,66	2,7

equiv./liter (Fig. 1). We carried out experiments in hydrochloric acid of about 1 N.

The optimum concentration of diethyldithiophosphoric acid is 0.2%, while that of the stannous chloride is 0.5%.

The absorption curve of a benzene extract, which was obtained on a Lange type photocolorimeter, shows that maximum absorption occurs at 436 mμ (Fig. 2).

The molar extinction coefficients of solutions of the compound of rhenium with diethyldithiophosphoric acid are given in Table 1; these values show that benzene is the most suitable solvent.

The relation between rhenium concentration and the optical density of benzene solutions is not linear (Fig. 3).

The mean square deviation, found from a small number of observations [5], does not exceed ± 4%.

Cupric ions in amounts greater than 0.2 mg in the test solut interfere with the reaction; 0.6 mg arsenic, 2 mg ferric ions, less than 0.1 mg of antimony, and 0.01 mg molybdenum also interfere. One determination takes 15-20 min.

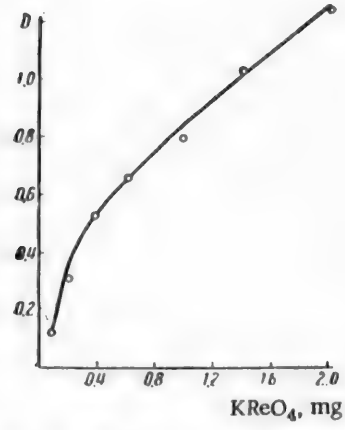


Fig. 3. The relation between optical density and rhenium concentration.

Analytical Procedure. Twenty ml of solution containing not less than 0.1 mg rhenium, 5 ml of hydrochloric acid (1 : 1), and 6 ml of a 1% aqueous solution of diethyldithiophosphoric acid are introduced into a 100 ml separating funnel. After shaking, the solution is allowed to stand for 10 min, 10 ml of benzene is added, the mixture shaken for one minute, and the layers allowed to separate out. The lower aqueous layer is run off. The upper benzene layer is centrifuged and transferred to a cuvette with a layer thickness of 30 mm. The optical density is measured at 436 mμ using a blue-green filter. Benzene is used as the reference solution. The rhenium content is determined from a calibration curve.

SUMMARY

Conditions have been established for the extraction photometric determination of rhenium using diethyldithiophosphoric acid.

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SPECTROCHEMICAL DETERMINATION OF SMALL AMOUNTS OF ALUMINUM AND SILICON IN NIOBIUM PENTOXIDE

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Several articles have been published in recent years on the spectrographic determination of impurities in niobium [1-3]. We are unaware, however, of any papers dealing with the determination of small amounts of aluminum and silicon.

Determination of less than 0.01 % of aluminum and silicon in niobium pentoxide is bound up with several difficulties: non-availability of sufficiently pure electrodes, the need for using special vessels, etc. In addition, the niobium spectrum has a complex structure and it is difficult to distinguish weak spectral lines of impurities on its background. In order to increase the sensitivity of impurity determination, we used the method of fractional distillation of samples with a carrier. Conditions can be chosen such that most of the aluminum and silicon present as impurities can be evaporated before the bulk of the niobium starts to evaporate. Use of a carrier ensures that the intensity of the impurity lines is increased. We tested Na_2CO_3, $CuCl_2$, Cu_2Cl_2 and AgCl as carriers. Cu_2Cl_2 and AgCl gave the best results, but cuprous chloride is comparatively unstable and is not very convenient to use.

AgCl was therefore used. Evaporation curves of the impurities and of niobium, with and without addition of silver chloride, are shown in Figs. 1 and 2. Addition of AgCl enhanced the fractionation effect. The boiling point of silver chloride is low (1550°). It is evident that AgCl, on evaporation, lowers the temperature of the spectrum excitation course, and this temperature is insufficient for intense evaporation of the slightly volatile niobium pentoxide.

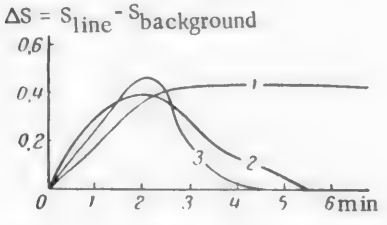

Fig. 1. Evaporation curves of (1) niobium, (2) silicon, and (3) aluminum without addition of silver chloride.

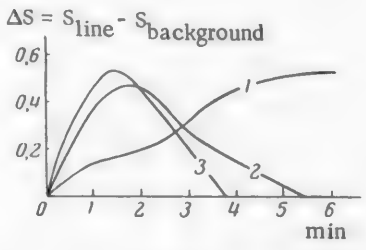

Fig. 2. Evaporation curves of (1) niobium, (2) silicon, and (3) aluminum with addition of silver chloride.

At the same time, the aluminum is chlorinated, and the readily volatile chloride is almost completely evaporated off in 2 min. Silicon is not chlorinated under these conditions, but the volatility of silicon is sufficient for most of it to evaporate before the niobium pentoxide starts to pass into the arc flame.

TABLE 1

Sample No.	Al content, %		Relative error, %	Si content, %		Relative error, %
	added	found		added	found	
1	0,001	0,00087	−13,0	0,005	0,0062	+24,0
2	0,0045	0,00523	+16,2	0,009	0,0105	+16,7
3	0,008	0,0092	+15,0	0,025	0,0257	+2,8
4	0,015	0,0155	+3,3	0,045	0,0501	+11,3
5	0,020	0,0224	+12,0	0,070	0,0617	−11,9
6	0,05	0,0462	−7,8	0,10	0,0960	−4
7	0,10	0,098	−2,0			
		Mean	±10			±12

TABLE 2

Sample No.	Al, 0,1 %		Al 0,001 %	
	I_{Al}/I_{Nb}	deviation from the mean	I_{Al}/I_{Nb}	deviation from the mean
1	0,536	+0,134	0,081	+0,002
2	0,412	+0,010	0,062	−0,017
3	0,338	−0,064	0,087	+0,008
4	0,366	−0,036	0,051	−0,028
5	0,320	−0,084	0,113	+0,034
6	0,442	+0,030	0,084	+0,005
7	0,403	+0,001	0,075	−0,004
8	0,398	−0,004	0,070	−0,009
9	0,395	−0,007	0,087	+0,008
10	0,412	+0,010	—	—
Mean	0,402	±0,048	Mean 0.079	±0,013
Reproducibility		±12 %	Reproducibility	±17 %

TABLE 3

Sample No.	Si 0,1%		Si 0,005%	
	I_{Si}/I_{Nb}	deviation from the mean	I_{Si}/I_{Nb}	deviation from the mean
1	0,340	−0,036	0,105	+0,006
2	0,405	+0,029	0,116	+0,017
3	0,347	−0,029	0,083	−0,016
4	0,381	+0,005	0,118	+0,019
5	0,291	−0,085	0,079	−0,020
6	0,372	−0,004	0,121	+0,022
7	0,401	+0,025	0,090	−0,009
8	0,415	+0,039	0,089	−0,010
9	0,395	+0,019	0,075	−0,024
10	0,413	+0,037	0,114	+0,015
Mean	0,376	±0,031	Mean 0.099	±0,0158
Reproducibility		±8,3%	Reproducibility	±159%

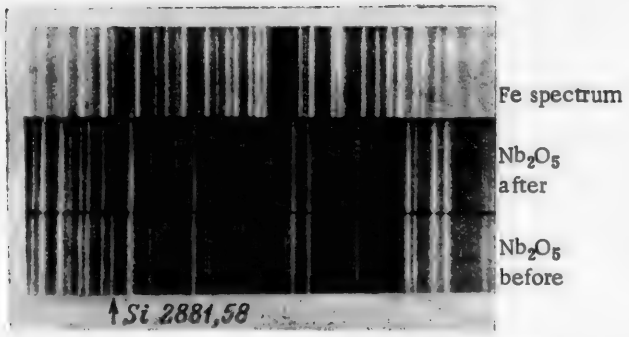

Fig. 3. Partial spectra of Nb_2O_5 before and after purification from silicon.

Determinations were carried out on a Hilger autocollimating spectrograph. An ac arc supplied by a DG-1 generator (18 amp at a voltage of 220 v) served as the light source. The spectrograph slit was 0.015 mm. The carbon electrodes had a diameter d = 6 mm. Samples were placed in a crater in the lower electrode, the crater was 3 mm deep and 3.5 mm in diameter. The upper electrode was sharpened to a truncated cone with an area of 1 mm. The inter-electrode gap was 3 mm.

The analytical lines were Al 3082.16 and Si 2881.58. The reference lines were Nb 3097.12 for aluminum, and Nb 2884.972 for silicon.

Exposure time was 2 min. A curve which was constructed within the coordinates log I/I_2 and log C [4] was used for the work. The background was taken into account. Platinum and stainless steel vessels replaced the glass and porcelain vessels when silicon was determined. The purity of the carbon electrodes was checked and the work was carried out with electrodes free from silicon and aluminum. In order to prepare standards, ordinary reagent grade niobium pentoxide was purified from aluminum by differential hydrolysis [5], the first fraction, which was almost free from aluminum, being taken. Niobium pentoxide was purified from silicon by dissolving an aliquot of the former in hydrofluoric acid and evaporating off the silicon as SiF_4. Part of the niobium pentoxide spectrum before and after purification from silicon is shown in Fig. 3.

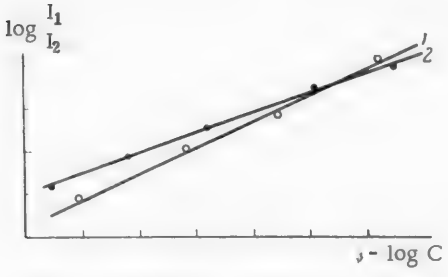

Fig. 4. Calibration curve (1) for silicon determination, (2) for aluminum determination.

Standards were prepared by adding a known amount of standard solutions of $Al_2(SO_4)_3 \cdot 16H_2O$ or $Na_2SiO_3 \cdot 9H_2O$ to an accurately weighed aliquot of spectrographically pure niobium pentoxide. After drying and calcining, the sample was mixed with a known amount of powdered silver chloride. The mixture was carefully mixed for one hour. Standards were prepared containing from 0.1 to 0.005% of Si and Al. The ratio $Nb_2O_5 \cdot AgCl = 2 : 1$. Twenty or 40 mg samples were taken. The part of the spectrogram shown in Fig. 4 gives an idea of the enhanced sensitivity of the aluminum line obtained on adding AgCl to the sample.

Calibration curves were constructed on the basis of the standards prepared (Fig. 4), and silicon and aluminum were then determined in a series of samples.

Table 1 contains results for the spectrographic determination of silicon and aluminum in niobium pentoxide.

These results show that during the determination of small amounts of aluminum (0.001%) and silicon (0.005%), the mean relative experimental error is not greater than ±10% for aluminum and ±12% for silicon.

Tables 2 and 3 contain results which characterize the reproducibilities of the relative intensities for two samples, each of which was photographed ten times, the lowest determinable concentrations of the two elements being taken.

The results given in these tables demonstrate the satisfactory reproducibility of the relative intensities.

The authors wish to thank Yu. V. Morachevskii for his advice and help in the work described here.

SUMMARY

A spectrographic method has been developed for the direct determination of small amounts of aluminum (down to 0.001%) and silicon (down to 0.005%) in niobium pentoxide; the experimental error is ± 12%.

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PHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH XYLENOL ORANGE

V. F. Luk'yanov and E. M. Knyazeva

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Original article submitted May 30, 1960

Xylenol orange is widely used at present as a complexometric indicator for the titration of many elements including zirconium [1]. Recently the use of xylenol orange for the photometric determination of zirconium and hafnium was described [2, 3]. We have used xylenol orange for the determination of zirconium in ores, the technique we used being considerably more simple than that suggested by Cheng [2, 3]. In 0.2-1 N hydrochloric acid, xylenol orange forms a red compound with zirconium ions (λ_{max} = 540 mμ). Absorption curves of the reagent and of its compound with zirconium are shown in Fig. 1. The zirconium compound forms almost instantaneously and is stable for several days. The photometric method involving xylenol orange ensures results with the highest reproducibility. The reagent is no less sensitive and selective than alizarin S, arsenazo I, arsenazo II, and pyrocatechol violet. Table 1 contains the permissible amounts of foreign elements in a final volume of solution of 50 ml.

Chloride, nitrate, perchlorate, sulfate (up to 100 mg), and tartrate (up to 5 mg) ions do not interfere with zirconium determination. Cr^{3+}, Bi^{3+}, fluoride, and phosphate ions interfere.

The photometric method is characterized with the speed with which it can be carried out; it consists of following. An aliquot of solution is evaporated with 5 ml of distilled hydrochloric acid to a volume of about 1 ml. The solution is transferred from the beaker to a 50 ml standard flask, 0.5 ml of a 0.01 M (about 0.8%) aqueous solution of xylenol orange is added and the volume made up to the mark with 0.5 N hydrochloric acid. The optical density is measured in a FÉKN-57 photo colorimeter using a No. 5 filter (λ = 536 mμ) and cuvettes with a layer thickness of 20 mm.

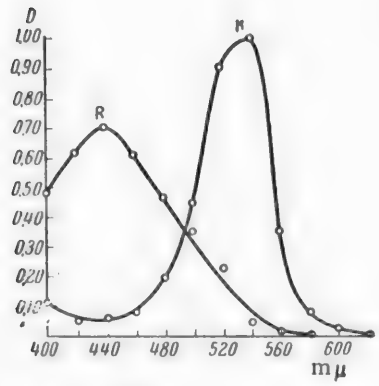

Fig. 1. Absorption curve of xylenol orange and of its complex with zirconium. R) $5 \cdot 10^{-5}$ M xylenol orange in 0.5 N HCl; K) $5 \cdot 10^{-5}$ M xylenol orange and $1 \cdot 10^{-4}$ M $ZrOCl_2$ in 0.5 N HCl; SF-4; cuvette 10 mm.

A calibration curve is constructed in the same way (Fig. 2).

Zirconium was determined in ores (Table 2) by the method described above.

Analytical Procedure. A 0.2-0.5 g aliquot of ore is fused with 5-10 g of sodium peroxide at 650° in a corundum crucible. The cooled melt is leached with hot water, and the liquid boiled for 5-10 min to destroy hydrogen peroxide (the volume of the solution should not be less than 250-300 ml). The solution is filtered through a fine filter (blue band) and the first portions of filtrate tested for absence of hydrogen peroxide (the filtrate is acidified with sulfuric acid and tested with Ti). The precipitate on the filter is washed 3-4 times with 5% sodium hydroxide, once or twice with water, and then dissolved in hot 2 N hydrochloric

TABLE 1

Effect of Various Elements on the Determination of Zirconium by Xylenol Orange (C_{Zr} = = 50 μg in 50 ml)

Elements	Permissible amount, μg/50 ml	Ratio Zr : element	Elements	Permissible amount, μg/50 ml	Ratio Zr : element	Elements	Permissible amount, μg/50 ml	Ratio Zr : element
Fe^{3+}	50	1 : 1	Cu^{2+}	5000	1 : 100	Nd^{3+}	2000	1 : 40
Fe^{2+}	5000	1 : 100	Cd^{2+}	500	1 : 10	La^{3+}	1000	1 : 20
Al^{3+}	500	1 : 10	Cr^{3+}	50	1 : 1	TiO^{2+}	1000	1 : 20
Bi^{3+}	50	1 : 1	Pb^{2+}	5000	1 : 100	UO_2^{2+}	200	1 : 4
Ni^{2+}	200	1 : 4	Sn^{2+}	1000	1 : 20	WO_4^{2-}	1000	1 : 20
Co^{2+}	2000	1 : 4	Sn^{4+}	500	1 : 10	MoO_4^{2-}	1000	1 : 20
Zn^{2+}	1500	1 : 3				VO_3^-	2000	1 : 40

• Reduced with 10 mg ascorbic acid.

TABLE 2

Determination of Zirconium in Ores

Zr found, %			Zr found, %		
with xylenol orange		with arsenazo III [4]	with xylenol orange		with arsenazo III [4]
0,050	0,052	0,054	0,33	0,33	0,28
0,060	0,061	0,058	0,33	0,32	0,30
0,075	0,076	0,074	0,050	0,050	0,042
0,42	0,42	0,46	0,055	0,055	0,057

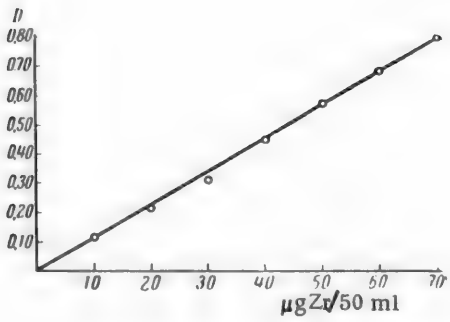

Fig. 2. Calibration curve for determination of zirconium with xylenol orange (20 mm cuvette).

acid. The solution is transferred to a 200-250 ml standard flask, and its volume made up to the mark with 2 N hydrochloric acid. An aliquot of this solution is taken (5 or 10 ml) and the procedure outlined above then followed.

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DETERMINATION OF SMALL AMOUNTS OF NIOBIUM IN ORES CONTAINING TITANIUM, TUNGSTEN, MOLYBDENUM, AND CHROMIUM•

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Original article submitted July 13, 1960

Good results are obtained when manganese dioxide is used as a collector for separating small amounts of niobium. This collector is used for the analysis of ores with a complex composition. The following analytical procedure is recommended. A 0.1-0.2 g aliquot (depending on the niobium content) is fused in a nickel or iron crucible with 5-10 g of sodium hydroxide. The melt is leached with water, the solution plus residue is boiled for 2-3 min and the residue filtered off on a fine filter and washed 3-5 times with 2% NaOH. The filtrate contains Cr, W, Mo, Sn, Si, and Al, while the residue contains Nb, Ta, Ti, and Fe. When the tungsten and chromium contents are high, the hydroxides are reprecipitated with sodium hydroxide. The filter plus residue, which has been washed with caustic solution, is wrapped round the edge of the beaker and the residue is washed off with a solution of sulfuric acid (2 : 250) to which several drops of hydrogen peroxide has been added; the filter is then discarded. Six to eight ml of sulfuric acid (1 :2) is added to the contents of the beaker and the whole boiled to destroy H_2O_2. One ml of 1 N manganese sulfate is added to the cooled solution, followed by 2 g of ammonium or potassium persulfate. The volume of the solution should be about 200 ml. The beaker is placed on a hot plate.

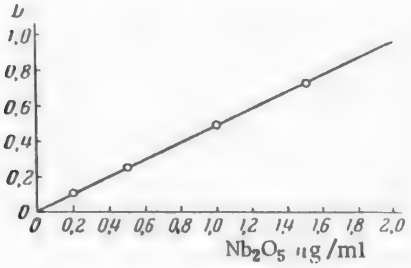

Fig. 1. Calibration curve for determination of niobium with thiocyanate and acetone at 360 mμ in a cuvette with a layer thickness of 3 cm.

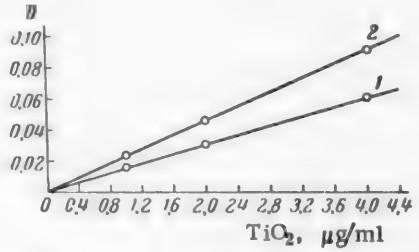

Fig. 2. Correction curve for titanium during determination of niobium. 1) Titanium with thiocyanate and acetone; 2) titanium with hydrogen peroxide (360 mμ, cuvette 3 cm).

The solution plus deposited manganese dioxide is boiled for 7-10 min, and, after being allowed to stand for some time, the precipitate is filtered off through a small fine filter and washed with dilute sulfuric acid (2 : 250). The filtrate contains Mo, Ti, Cr, Zr, and Fe. The niobium is isolated quantitatively with the manganese dioxide [1].

• Read at the conference on the analysis of rare and semiconducting elements held in Moscow, December 8, 1959.

TABLE 1

Comparative Results for the Determination of Niobium by Various Methods (%)

Test material	Chemical methods of analysis		Physical methods of analysis	
	recom. MnO_2 method	Bykov's method	spectrographically	x-ray spectrographically
Columbite ore	0,006	0,005	0,004	0,007
" "	0,028	0,027	0,026	0,027
" "	0,009	0,009	0,009	0,011
" "	0,020	0,020	0,020	0.022
" "	0,013	0,012	0,012	0,013
" "	0,009	0,008	0,008	0,010
" "	0,005	0,005	0,005	0,005
" "	0,060	0,060	0,060	0,080
Zirconium ore	0,110	0,110	0,110	0,150
Eudialite ore	0,250	0,250	0,250	0,300
Pyrochlore ore	0,345	0,350	0,350	0,340
Concentrate from columbite ore	0,480	0,480	0,500	0,520
Concentrate from pyrochlore ore	0,760	0,780	0,800	0,840
" " " " "	1,970	2,000	2,250	2,000

TABLE 2

Determination of Niobium in the Presence of Tungsten and Molybdenum

Nb_2O_5 content (mean 5 repeat determinations)	WO_3 added		Mo added		Nb_2O_5 found by the recommended method, %	Deviation from the mean arithmetic value, %	
	mg	ratio Nb_2O_5:WO_3	mg	ratio Nb_2O_5:Mo		absolute	relative
0,027	9,37	1 : 69	8,5	1 : 63	0,026	0,001	—3,71
0,033	9,37	1 : 56	8,5	1 : 51	0,031	0,002	—6,03
0,031	9,37	1 : 60	8,5	1 : 55	0,030	0,001	—3,55
0,031	9,37	1 : 60	8,5	1 : 55	0,030	0,001	—3,55
0,029	9,37	1 : 64	8,5	1 : 58	0,030	0,001	+3,44
0,026	9,37	1 : 74	8,5	1 : 65	0,027	0,001	+3,84

Reprecipitation is carried out as follows to effect more complete separation of interfering elements. The manganese dioxide is washed off the filter into the beaker in which the first precipitation was carried out, and the funnel with the filter placed over the beaker. The filter is washed with a sulfuric acid solution (2 : 250) containing a few drops of hydrogen peroxide, and then with pure water until there is no hydrogen peroxide left on the filter. The filtrate which has a volume of about 200 ml contains 6-8 ml of sulfuric acid (1 : 2). The filter is used for the next filtration. The solution is boiled to destroy hydrogen peroxide, it is then cooled, and precipitation with persulfate repeated as described above.

The manganese dioxide precipitate containing the entrained niobium is fused with 1,5-3 g of sodium bisulfate. After cooling, the melt is dissolved in 15% tartaric acid solution and the volume made up to 25 or 50 ml. The final tartaric acid concentration is 7,5%.

Niobium is determined photometrically by Freund and Levitt's method [2], in an acetone–water medium with thiocyanate at 360 mμ (filter No. 1, FEK-N photocolorimeter) using a 3 cm cuvette. The niobium content is calculated by means of a calibration curve (Fig. 1). If titanium has not been completely removed, a correction obtained from a curve (Fig. 2) is applied.

The thiocyanate method for niobium [3] is very sensitive. In the case of a 2 g aliquot of ore containing 0.005% Nb_2O_5, and a dilution of 25 ml, a 10 ml aliquot contains 0.04 mg Nb_2O_5. A solution with a volume of 50 ml (0.8 μg/ml) has an optical density of 0.4. Accordingly, a 5 ml aliquot can be used for a determination. By increasing the weight taken to 5 g, the sensitivity is increased and it is possible to determine thousandths of a percent. Table 1 contains the results of niobium determinations.

For determination of niobium in samples of columbite and zirconium ores by physical methods, an enrichment technique was used beforehand (enrichment factor $K_{enrich.} = 30\text{-}50$). No enrichment was used for the other ores.

The analytical method including alkali decomposition and precipitation of niobium in a sulfuric acid medium is suitable for ores containing tungsten, molybdenum, and chromium. In order to confirm this, a known amount of tungsten and molybdenum concentrates was added before fusion to an aliquot of ore (0.5 g) with a known niobium content. After two precipitations with MnO_2, the niobium was determined by the thiocyanate method. As Table 2 shows, the results obtained for niobium are in complete agreement with the results obtained for these sample before addition of tungsten and molybdenum.

SUMMARY

During analysis of ores containing titanium, tungsten, molybdenum, and chromium, small amounts of niobium are separated by coprecipitation with manganese dioxide. A photometric thiocyanate finish is used for determining the niobium.

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DETERMINATION OF PALLADIUM AND NICKEL, AND OF PALLADIUM AND COPPER IN EACH OTHERS PRESENCE

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Original article submitted July 4, 1960

Previous papers have dealt with formation of compounds between β-hydroxynaphthaldehyde and palladium and other divalent cations [1], and with the quantitative determination of palladium with this aldehyde in the presence of a number of cations [2]. Since β-hydroxynaphthaldehyde precipitates palladium in acid media (pH 2.5-3), while it precipitates copper and nickel at pH > 7, it should be possible to determine palladium simultaneously with one of these elements without preliminary separation. The classical dimethylglyoxime method only permits determination of palladium and nickel. Determination of copper by this aldehyde has been described previously [3]; nickel has not been precipitated quantitatively by β-hydroxynaphthaldehyde.

Experimental. Palladium nitrate was prepared by dissolving an accurately weighed aliquot of palladium wire (0.1 g) in 2-3 ml concentrated HNO_3, sp. gr. 1.43. Nickel and cupric nitrates were prepared by dissolving accurately weighed aliquots of the pure metals (0.2 g) in 2 ml HNO_3, sp. gr. 1.39. The solutions were transferred to standard flasks and made up to the mark with water.

β-Hydroxynaphthaldehyde was synthesized from β-naphthol and chloroform in an alcoholic-alkali medium; it was distilled under vacuum and recrystallized from alcohol; m. p. 80-81° [4].

Determination of Palladium and Nickel. Five ml of palladium nitrate solution and 10 ml of nickel nitrate solution pH 2.5-3 are mixed. The mixture is diluted with an equal volume of alcohol. Palladium is precipitated with 5 ml of a 1% alcoholic solution of the reagent. On mixing with a rod, a yellow precipitate separates out. The latter is allowed to stand for 20-25 min at room temperature, it is then kept for 5 min on a water bath at 70°; it is next filtered off through a Schott No. 2 crucible, washed with 50% alcohol and dried at 110° for 25-30 min. The filtrate is quantitatively transferred from the Bunsen flask to a beaker; to the latter is added a few drops of 0.25 N sodium hydroxide, and crystalline sodium acetate added to adjust the pH to 7.2-7.5, the liquid brought up to the boil, and precipitation effect by addition of 10 ml of heated 1% alcoholic solution of the reagent. The yellow-green precipitate is allowed to stand for 25 min, filtered through a Schott No. 4 crucible, washed with 50% alcohol, and dried at 150° for 40-45 min. The conversion factor to palladium is 0.2377, while the conversion factor to nickel is 0.1464.

Palladium and copper are determined in a similar way in a solution containing both elements. After filtering off the palladium precipitate, the pH is increased by adding small amounts of 0.25 N NaOH and sodium acetate, or by adding ammonium hydroxide as described earlier [3]. The use of dilute alkali and sodium acetate for adjusting the pH to 7.3-7.5 has the advantage that the solutions do not darken. On the other hand care must be taken during neutralization in order to avoid formation of hydroxides.

As the results given in Tables 1 and 2 show, the experimental errors do not exceed the permissible values.

TABLE 1

(5.00 mg Pd taken)

Taken, mg	Found, mg		Absolute error, mg	
Ni	Pd	Ni	for Pd	for Ni
10,00	5,10	10,25	+0,1	+0,25
10,00	5,00	10,20	0,00	+0,20
5,00	4,90	5,00	—0,10	0,00
10,00	5,20	9,88	+0,20	—0,12
9,83	5,10	9,80	+0,10	—0,03

TABLE 2

(5.00 mg Pd taken)

Taken, mg	Found, mg		Absolute error, mg	
Cu	Pd	Cu	for Pd	for Cu
5,00	4,90	5,10	—0,10	+0,1
10,00	5,10	10,2	+0,10	+0,2
5,00	5,00	5,16	0,00	+0,16
10,00	5,00	9,90	0,00	—0,1

SUMMARY

A method is suggested for the determination of palladium and nickel, and of palladium and copper on one aliquot. Palladium is precipitated with β-hydroxynaphthaldehyde at pH 2.5-3, while nickel and copper are precipitated at pH 7.2-7.5.

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THE USE OF NAPHTHOL YELLOW INSTEAD OF URANYL NITRATE IN THE STANDARD METHOD OF DETERMINING THE OXIDIZABILITY OF COMMERCIAL ETHANOL

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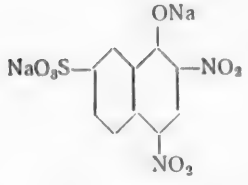
Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 2,
p. 255, March-April, 1961
Original article submitted

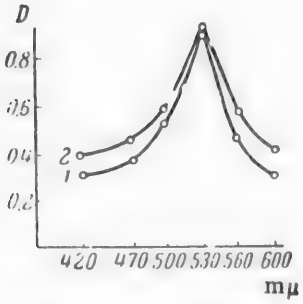
The oxidizability of commercial ethanol produced by fermentation is determined, according to GOST 5964-51, by comparing its color after adding a known amount of potassium permanganate solution to it, with the color of a standard solution for preparation of which uranyl nitrate is used.

Uranyl nitrate can be replaced by naphthol yellow which is more readily available; this reagent,



, is commercially produced in the USSR. The dye is readily soluble in water, and its solutions are stable and chemically inert and have a yellow color in the pH range 1 to 13.

Aqueous solutions of uranyl nitrate and naphthol yellow have similar absorption curves, and their maxima are located at the violet edge of the visible part of the spectrum. At the same time, the absorption intensity of naphthol yellow solution is three orders higher (2.4×10^3) than that of isomolar solutions of uranyl nitrate. From these results it is possible to calculate the naphthol yellow concentration for which its solutions will have equal optical density to that of uranyl nitrate in the standard solution; we found that the requisite concentration is 3×10^{-5} M.



Absorption curves of standard solutions. 1) Uranyl nitrate + + $CoCl_2$; 2) naphthol yellow + + $CoCl_2$.

Preparation of a standard solution containing naphthol yellow instead of uranyl nitrate reduces to mixing 5 ml of the first solution with 7 ml of the second solution, and making up the volume to 100 ml with distilled water.

First Solution, fifty g of pure cobalt chloride is dissolved in a one liter standard flask; second solution, 0.0118 g of naphthol yellow is dissolved in a one liter standard flask.

Absorption curves for a solution prepared exactly as specified in GOST (Curve 1) and for a solution in which uranyl nitrate is replaced by

naphthol yellow (Curve 2) are shown in the Fig. They clearly show the identity of the light absorption of standard solutions prepared from uranyl nitrate and naphthol yellow.

Standard solutions prepared with this dye are stable with time; the optical density hardly changes at all in the course of 20-25 days.

An attempt to use the standard technique for determining the oxidizability of alcohol from the Saratov synthetic alcohol plant proved unsuccessful: on adding potassium permanganate to the test alcohol solution the solution immediately became brown; this indicates the presence of a large amount of readily oxidizable materials in the synthetic alcohol.

SUMMARY

It has been shown that naphthol yellow can be used instead of uranyl nitrate for preparing the standard solution used for determining the oxidizability of alcohol.

PETR NIKOLAEVICH PALEI

(On his sixtieth birthday)

On October 19, 1960,Petr Nikolaevich Palei,one of our outstanding analytical chemists,celebrated his sixtieth birhday.

P. N. Palei was born October 19, 1900 in Zhitomir in the Ukraine. While still student in Leningrad State University,in 1922,he taught chemistry in the Artillery Pyrotechnical School, and started,in 1924,to carry out hydrochemical research using the new—at that time—colorimetric and electrometric methods of determining pH, in connection with the photochemical activity of plants. From 1926 he also worked in the Geological Committee on the Chemistry of Natural Water

P. N. Palei set up new types of field hydrochemical laboratories and established the chemical composition of water from many sources in the USSR. From 1929 to 1937 he was the head of the hydrochemical laboratory of the All-Union Institute of Health Resort Administration. Among the numerous hydrochemical researches of P. N. Palei, particular mention should be made of his work on the study of the hydrogen sulfide water of Psekuns and Matsesta, the mineral waters of Osetni, Dagestan, Kareliya, the Far East, and the Ural, on the geochemistry of lake loam from Trans Ural, Crimea, and the Far Eastern Region, as well as his work on the escape of hydrogen sulfide from Matsesta water, and his studies on sulfide-carbonate equilibria.

P. N. Palei has also published a number of papers on balneotherapy; a method which he developed for the production of synthetic hydrogen sulfide water has been adopted in the health resorts of the Soviet Union. He has published a number of textbooks on field hydrochemical analysis.

In 1937 he switched over to work in the Biogeochemical Laboratory of the Academy of Sciences, USSR (subsequently the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR), where he studied the distribution of rare and dispersed elements in mineral waters.

In 1937-1939 P. N. Palei developed methods for the determination of small amounts of beryllium.

In the course of the last 15 years, working in the Institute of Geochemistry and Analytical Chemistry, he has given most of his attention to improving, developing, and introducing new precision methods of analysis into practice. At the same time,he has also carried out a thorough and systematic study of the analytical chemistry of the actinides.

He has published more than 200 papers. He maintains a close connection with many industrial laboratories and enterprises and gives them his help. He has instructed a large number of young scientists, particularly in precision methods of analysis and in the analytical chemistry of the actinides. He also carries out social duties,

being a member of the Commission on Analytical Chemistry. He has been awarded prizes for his fruitful work.

The Commission on Analytical Chemistry, the Editorial Board of the Journal of Analytical Chemistry, analytical chemists, his co-workers, and students wish to congratulate him on his many years of fruitful scientific work.

NEW REAGENT FOR THE LUMINESCENT DETERMINATION OF MAGNESIUM

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 2,
inside back cover.

The All-Union Scientific-Research Institute of Chemical Reagents (IREA) has synthesized a new reagent for the luminescent determination of magnesium; this reagent—lumomagneson—permits determination of 0.02 μg Mg in 5 ml in an aqueous medium at pH 10.0. Equal amounts of foreign cations do not interfere with magnesium determination. The permissible ratio of Mg : Ca = 1 : 100.

Organizations and enterprises wishing to test the new reagent can get a free sample and instructions for its use by sending a request to the following address: Moscow, Samokatnaya Ulitsa, Dom 4a—Institute of Chemical Reagents.

Lumomagneson is not being produced on the plant scale at the moment, and in order to decide whether it is worth producing on a commercial scale, the Institute of Chemical Reagents earnestly requests all organizations and enterprises to let them know two months from receipt of samples what they think of its practical value.

The Institute will give advice on all problems connected with the use of lumomagneson.

A CONFERENCE ON EXTRACTION IN ANALYTICAL CHEMISTRY

Translated from Zhurnal Analiticheskoi Khimii, Vol. 16, No. 2,
back cover.

The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, and the Commission on Analytical Chemistry intend to convene a conference on extraction in analytical chemistry, in Moscow in December 1961.

The conference will discuss reports on the use of extraction in analytical chemistry, in particular, on the following lines:

1. Theoretical questions of extraction.

2. General methodological questions of the use of extraction in analytical chemistry (new principles of extraction separation, extraction–photometric method, the study of complex formation by extraction methods, and the use of extraction in radiochemical analysis).

3. The application of extraction methods for the analysis of various materials.

4. New extractants and extraction apparatus.

5. Questions relating to the classification and terminology of extractions processes and methods.

The Institute of Geochemistry and Analytical Chemistry, and the Commission on Analytical Chemistry invite workers in scientific-research institutes, universities, and industrial laboratories to take part in the work of the conference.

Titles and annotated reports (1-2 typewritten sheets) as well as requests for tickets to attend the conference should be sent to the organizing committee of the conference before July 15, 1961 at the following address: Moscow, V-133, Vorob'ev Road, 47a, Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, Organizing Committee on Extraction.

The exact date of the conference will be announced later.

Organizing Committee

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

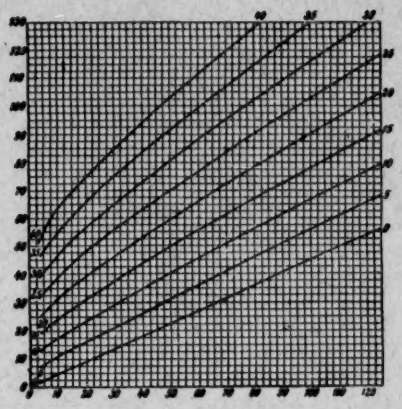
Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections) — Life Sciences	American Institute of Biological Sciences	112	1	1957
		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections) — Life Sciences	American Institute of Biological Sciences	112	1	1957
		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology — Chemical Sciences	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry — Chemical Sciences	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry — Chemical Sciences	Consultants Bureau	112	1	1957
		Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections) — Earth Sciences	American Geological Institute	124	1	1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry — Earth Sciences	Consultants Bureau	106-123	1 6	1957- 1958
		Proceedings of the Academy of Sciences of the USSR, Sections: Geology — Earth Sciences	Consultants Bureau	106-123	1 6	1957- 1958
		Doklady Soviet Mathematics — Mathematics	The American Mathematics Society	131	1	1961
		Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections) — Physics	American Institute of Physics	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections) — Physics	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union	1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute	1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1 1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3 1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1 1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1 1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1 1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1 1958
	Metallurg	Metallurgist	Acta Metallurgica		1 1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1 1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1 1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6 1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1 1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1 1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1 1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1 1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada		
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1 1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1 1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1 1959
	Stal'	Stal (In English)	Iron and Steel Institute		1 1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1 1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4 1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1 1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1 1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1 1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1 1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1 1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd	48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.	4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*	1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*	1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*	1	1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1 1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1 1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1 1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7 1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1 1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1 1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1 1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1 1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1 1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1 1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1 1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.



TABLES AND NOMOGRAMS OF HYDROCHEMICAL ANALYSIS

by I. Yu. Sokolov

Translated from Russian

(c/b) CONSULTANTS BUREAU
227 W. 17 ST., NEW YORK 11, N. Y.

Upon completion of analytical experiments, every research chemist, whether he uses a "test tube" or a "пробирка," must calculate his findings in the international language of figures in two forms (weights and equivalents), and often three (weights, equivalents and percent-equivalents), and then compare experimental data with theoretical values.

Technicians and statisticians working with the results of hydrochemical analyses performed at different times by different laboratories inevitably face the problem of converting their figures to one system.

All such calculations are considerably simplified by the use of the tables and nomograms in this book, originally published by the State Scientific and Technical Press for Literature on Geology and the Conservation of Mineral Resources, Moscow.

All the tables and nomograms are based on analytical results expressed in the form widely used in hydrogeological practice—milligrams per liter (weight form) and milligram-equivalents per liter (equivalent form). For calculation of percent-equivalents, the sum of cation equivalents and the sum of anion equivalents are taken as 100% each. Several new tables are presented for the first time, and the many tables for converting water-analysis results from one form to another make it possible to find the milligram-equivalents for any practically possible content of a component in water, accurate to the second decimal place, and the weight content of substances to tenths of a milligram.

CONTENTS

Introduction
Tables for converting water-analysis results from one form to another
I. Table for converting hardness, expressed in German degrees, into milligram-equivalents
II. Table for converting milligram-equivalents of Ca^{2+}, Mg^{2+} and HCO_3^- into German degrees of hardness
III. Tables for converting milligrams into milligram-equivalents
IV. Tables for converting milligram-equivalents into milligrams
V. Tables for converting oxides to ions
VI. Tables for converting nitrogen into nitrogen-containing ions
VII. Table for converting milligrams of NH_3 into milligrams of NH_4^+
VIII. Table for converting oxidizability with milligrams of $KMnO_4$ into milligrams of O
Factors for converting the results of water analysis from one form into another
Average value of activity coefficient f_{av}
Nomogram for calculating percent-equivalents
Nomogram for calculating pH from given values of free CO_2 and HCO_3^-
Calculation of aggressive carbon dioxide
Relation between different forms of weak acids in natural waters at different pH values and ionic strengths μ
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4,5-Dimethyl-2-Furaldehyde
2,5-Furandimethanol
2,2'-Methylenedifuran
N,N-Diethyl-2-Furamide
5-Carboxy-2-Furanacetic Acid
Methyl 5-Formyl-2-Furoate
4-(5-Methyl-2-Furyl)-3-Buten-2-One
4-(5-Methyl-2-Furyl)-2-Butanone
2-(5-Methylfurfurylamino)Pyridine
5-Nitrofurfuryl Alcohol
5-(Hydroxymethyl)-2-Furoic Acid

3-Aminopyridine
5-(Benzylsulfonylmethyl)-2-Furoic Acid
4-(5-Benzyl-2-Furyl)-3-Buten-2-One
Benzofuran (Coumarone)
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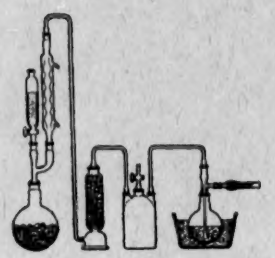
2,3-Dimethylindole-5-Carboxylic Acid
Tetrahydro-2,5-Furandimethanol
N,N-Diethyltetrahydrofurfurylamine
Indazole
Indole-3-Carboxaldehyde
3-(3-Piperidinopropyl)Indole
Indole-3-Acetic Acid (Heterouxin)
2,3-Dihydro-2-Methylbenzofuran
5-Methylisatin
2-Methylindole-3-Propionic Acid
2-Isoindolineethanol



SYNTHESES OF HETEROCYCLIC COMPOUNDS

Edited by
A. L. MNDZHOIAN

TRANSLATED FROM RUSSIAN

Volumes 1 and 2

The lack of a practical guide to the laboratory preparation of heterocyclic compounds is being met by this series of collections of synthesis methods, originally published by the Armenian Academy of Sciences.

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